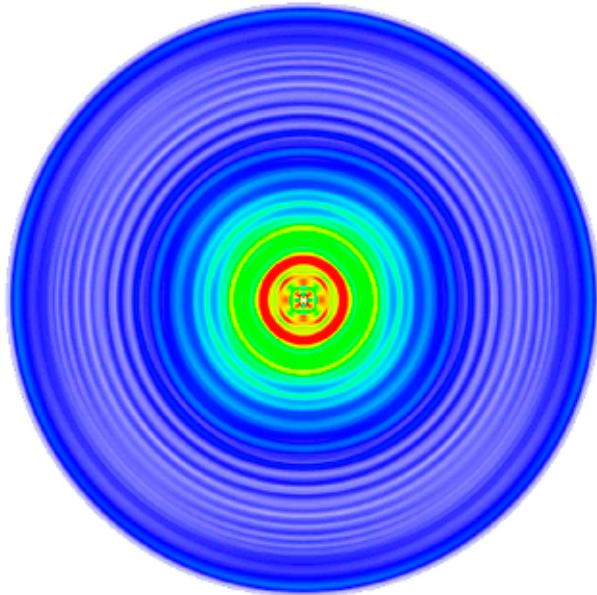
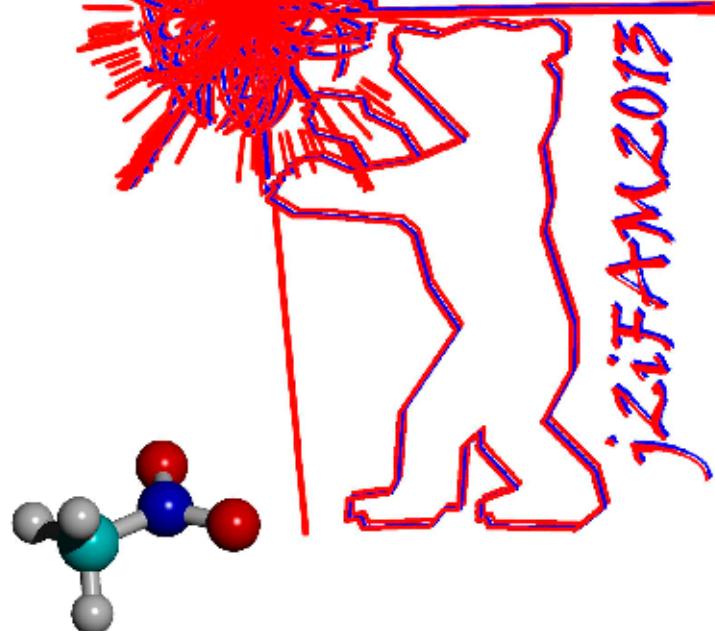


V Jornadas de Jóvenes Investigadores en Física Atómica y Molecular



February, 13rd - 15th 2013 Madrid, Spain

**Physics of Aggregates
Reaction Dynamics
Quantum Chemistry
Surface Physics
Atomic and Molecular Collisions**

**Ultracold Atoms and Molecules
Nanomaterial Science
Spectroscopy and Excited States
Quantum Information**



<http://www.ucm.es/centros/webs/j2ifamv/>



**Salón de actos
Facultad de Ciencias Químicas
UCM**



UNIVERSIDAD COMPLUTENSE DE MADRID
FACULTAD DE QUÍMICA y FACULTAD DE FÍSICA



V Jornadas de Jóvenes Investigadores en Física Atómica
y Molecular
(J2IFAM 2013)

Madrid, February, 13rd-15th 2013

Index

About J2IFAM	5
Organizing Committee	7
Sponsors and Supporters	9
Scientific Program	11
Abstracts	17
Oral Presentations	17
Marta González	18
Elena Moreno Atahonero	19
Rui E. F. Silva	20
David Ayuso	21
David Ayuso	22
Maite Cueto	24
Ignacio López	25
Juan J. Nogueira	26
Estefanía Lopez	27
Silvia Acosta-Gutiérrez	28
Humberto Jr. Silva	29
Maitreyi Robledo	31
Rocio Rodríguez-Cantano	33
Virginia Ovejas	34
Marta Fernández-Fernández	35
Patricia Écija	36
Imanol Usabiaga	37
Estíbaliz Méndez	38
Roberto Antonio Fernández	39
Alexandre Zanchet	40
Alba Maria Jorge	41
Patricia Barragán	42
David Ferro-Costas	43
Jorge González	44
Estefania Rossich Molina	45
Chiara Paris	46
Ricardo Perez Tudela	47
Diego Herráez	49

Patricia Vindel-Zandbergen	50
Montserrat Vallejo López	51
Rafael Delgado López	52
Posters	53
David Ayuso	54
Elisa Corda	55
Martin Heimsoth	56
Dariusz G. Piekarski	57
Margarita Hernández Gonzalez	59
M. Jiménez-Redondo	60
Maite Cueto	61
Elena Moreno	62
Cristina Sanz Sanz	63
List of Participants	65

About J2IFAM

Jornadas de Jóvenes Investigadores en Física Atómica y Molecular (J2IFAM) was born in Madrid on December, 12th 2008, in order to establish a meeting point where graduate students and recent post-docs could discuss their research advancements in physics and chemical physics. This first edition was held at Instituto de Física Fundamental (CSIC) and was financed by CSIC (Consejo Superior de Investigaciones Científicas), GEFAM (Grupo Especializado de Física Atómica y Molecular) and RSEF (Real Sociedad Española de Física).

Now we can look back to a five year old stable tradition of J2IFAM conferences, which so far took place in Madrid, Barcelona, Santiago de Compostela, Granada, and is now coming back to Madrid. The first edition of the J2IFAM conference was held on one day. Today, we are glad to receive about 42 participants.

Organizing Committee

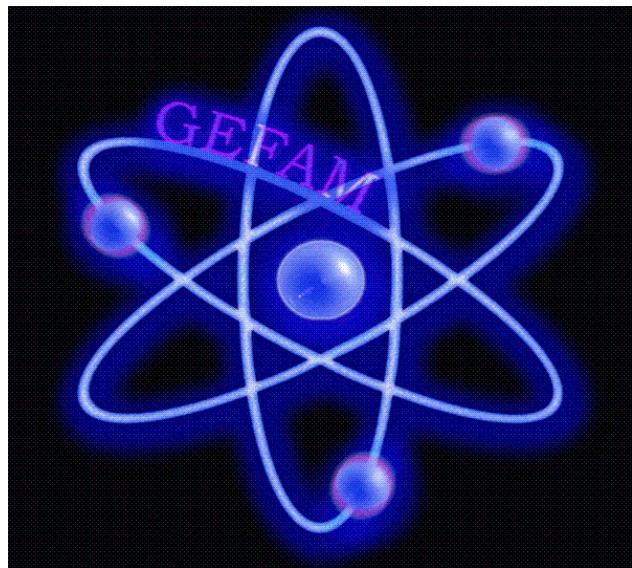
The IV J2IFAM is organized by eight Ph.D. students from the Complutense University Madrid:

- Javier Rodríguez Díaz
- Marta González González
- Ma Eugenia Corrales Castellanos
- Garikoitz Balerdi Villanueva
- Martin Heimsoth

The organizers can be contacted by email at j2ifam@fis.ucm.es or j2ifam@quim.ucm.es.

Sponsors and Supporters

We gratefully acknowledge the generous support of the following institutions:



Scientific Program

Wednesday, February 13th

Hour	Speaker	Title
15:00		Registration
17:00	Welcome	Opening Session: Chemistry Faculty Dean, Reyes Jiménez Aparicio
Session A. Chair: Javier Rodriguez		
17:20	Marta González	Stereodynamics as a means to disentangle Photochemical mechanisms
17:45	Elena Moreno Atahonero	Procesos colisionales de H ₂ O + He en jets supersónicos por espectroscopia Raman
18:10	Rui E. F. Silva	Electron and nuclear dynamics of H ₂ ⁺ induced by intense ultrashort laser pulses
18:35	Garikoitz Balerdi	Strong field control of predissociation dynamics
19:00	David Ayuso	Vibrationally resolved photoionization spectra of small molecules

Thursday, February 14th

Hour	Speaker	Title
Session B. Chair: Cristina Sanz		
10:00	Maite Cueto	A new way to enhance sensitivity in stimulated Raman spectroscopy: Hollow-core photonic crystal fibers
10:25	Ignacio López	Low-Order harmonic generation in nanosecond laser ablation plasmas of carbon containing materials
10:50	Juan Jose Nogueira	Ab initio Force Field for Liquid and Vitreous Silica
11:15	Estefanía Lopez	Ion-Molecule Reactions with alkali metals
11:40		<i>Coffee Break</i>
Session C. Chair: Estíbaliz Méndez		
12:10	Silvia Acosta-Gutiérrez	Optimal covering of C_{60} fullerene by rare gases
12:35	Humberto Silva	Theoretical treatment of the fragmentation dynamics of excited highly charged fullerenes
13:00	Maitreyi Robledo	Density Functional Theory on the interaction between metals and C_{60}
13:25	Rocio Rodríguez	Study of Ca impurity in helium clusters
13:50		<i>Lunch</i>
Session D. Chair: Mariu Corrales		
15:30	Virginia Ovejas	Ultrafast Photophysics of Simple Aromatic Chromophores
15:55	Marta Fernández	Femtosecond ultrafast evolution of Imidazole and Pyrrole after electronic excitation
16:20	Patricia Écija	Rotational Spectra of Sugars: Ribose and Fructose
16:45	Imanol Usabiaga	Espectroscopía electrónica con resolución de masas de β -Fenil-DGlucopiranosa·D-Glucosa en expansiones supersónicas
17:10	Estíbaliz Méndez	Structure of Succinic Acid in the gas phase
17:40		Poster Session
21:30		<i>Dinner</i>

Friday, February 15th

Hour	Speaker	Title
Session E. Chair: Juan José Nogueira		
10:00	Roberto Antonio Fernández	Clustering en experimentos de imagen mediante cadenas de Markov (RankCompete)
10:25	Alexandre Zanchet	Theoretical study of the reaction of S+ with vibrationally excited H ₂
10:50	Alba Maria Jorge	Charge-exchange and ionization cross sections for atomic collisions relevant in fusion research
11:15	Patricia Barragán	Full-dimensional ab initio potential energy surface and dynamics for the H7+ cluster
11:40	<i>Coffee Break</i>	
Session F. Chair: Roberto Antonio		
12:10	David Ferro Costas	Why does C-O lengthen and C pyramidalize in the $n\pi^*$ state of formaldehyde? Expanding QTAIM to Excited States
12:35	Jorge González Rodriguez	DNA base – Amino acid interactions: a theoretical study
13:00	Estefanía Rossich	Initial approaches on Dynamic of Fragmentation of L- α -Alanine ⁺²
13:25	Chiara Paris	Theoretical Study of the ionization and fragmentation of positively charged polycyclic aromatic hydrocarbons
13:50	<i>Lunch</i>	
Session G. Chair: Ute Mustermann		
15:30	Ricardo Perez Tudela	Chemical reaction rate coefficients from Ring Polymer Molecular Dynamics
15:55	Diego Herráez	Anomalous Angular Distributions in H + D ₂ → H + HD reaction
16:20	Patricia Vindel	Quantum control with the non-resonant Stark effect: manipulating the singlet-triplet transition in ion strings
16:45	Montserrat Vallejo	Rotacional Spectra and Ab Initio Modeling of Monolignols
17:10	Rafael Delgado López	

Thursday, February 3rd 19:00-20:00

Friday, February 4th 17:00-18:00

Poster	Author	Title
P1	David Ayuso	Vibrationally resolved k-shell photoionization spectrum of BF ₃
P2	Elisa Corda	Caracterización espectroscópica de los fármacos indometacina y ketorolac en disolución acuosa
P3	Martin Heimsoth	Chaos and macroscopic superpositions in a driven Bose gas
P4	Dariusz G. Piekarski	Fragmentation dynamics of excited amino acids in gas phase: glycine and β -alanine
P5	Margarita Hernández González	Fluorescence characterization of a drug delivery system based on a nanostructured porous silicon matrix loaded with the anti-tumoral drug emodin adsorbed on silver nanoparticles
P6	Miguel Jiménez-Redondo	Energy Distributions of Neutrals and Ions in H ₂ Low Temperature Plasmas
P7	Cristina Sanz Sanz	Global potential energy surface of H ₄ ⁺ system. Reactive collisions using QCT

Abstracts

Oral Presentations

Stereodynamics of the photodissociation of nitromethane at 193 nm: Unravelling the dissociation mechanism

M. G. González¹, J. D. Rodríguez¹, L. Rubio-Lago¹, and L. Bañares¹

¹Departamento de Química Física I, Facultad de Ciencias Químicas, Universidad Complutense de Madrid
E-mail: marta.glezglez@hotmail.com

The photodissociation of nitromethane at 193 nm is reviewed in terms of new stereodynamical information provided by the measurement of the first four Dixon's bipolar moments, $\beta_0^2(20)$, $\beta_0^0(22)$, $\beta_0^2(02)$ and $\beta_0^2(22)$, using slice imaging [1,2]. The measured speed-dependent $\beta_0^2(20)$ (directly related with the spatial anisotropy parameter β) indicates that after one photon absorption to the $S_3(2^1A'')$ state by an allowed perpendicular transition, two reactions pathways can compete with similar probability: a direct dissociation process yielding ground state CH_3 and $NO_2(1^2A_2)$ radicals, and a indirect dissociation through conical intersections in which NO_2 radicals are formed in lower lying electronic states. A particularly important result from our measurements is that the low recoil energy part of the methyl fragment translational energy distribution presents a contribution with parallel character, irrespective of the experimental conditions employed, that we attribute to parent cluster dissociation. Moreover, the positive values found for the $\beta_0^0(22)$ bipolar moment indicates a propensity for the fragment's recoil velocity and angular momentum vectors to be parallel.

[1] R. N. Dixon, J. Chem. Phys. (85), 1866 (1986).

[2] Michael P. Grubb, Michelle L. Warter, C. Daniel Freeman, Niclas A. West, Kelly M. Usakoski, Kurt M. Johnson, Jeffrey A. Bartz, and Simon W. North, J. Chem. Phys., (135), 094201 (2011).

Procesos colisionales de H₂O + He en jets supersónicos por espectroscopia Raman

E. Moreno, G. Tejeda, J.M. Fernández, y S. Montero

¹Departamento de Física Molecular, Instituto de Estructura de la Materia, CSIC, Madrid.

E-mail: Elena.moreno@csic.es

Las expansiones supersónicas de gases moleculares y de mezclas gaseosas, son de gran interés para las distintas ramas de la física, la química, la ingeniería o la astrofísica [1]. Las propiedades de estos sistemas difieren notablemente de las de un gas en equilibrio termodinámico, siendo necesario caracterizar las propiedades fluidodinámicas del jet. Para realizar los estudios cuantitativos de diferentes mezclas de H₂O+He en jets supersónicos se ha empleado espectroscopia Raman (Figura 1). Este método espectroscópico ha sido mejorado y adaptado para conseguir un diagnóstico preciso de los diferentes estudios. Una característica a destacar de estas expansiones de mezclas de H₂O +He, es que se han conseguido que estén libres de condensación. Trabajando con presiones parciales de agua en torno a 12 mbar y diferentes proporciones de He. De los experimentos realizados, se obtienen datos de densidades absolutas y poblaciones rotacionales a lo largo de las líneas de flujo. Se observa que la distribución de los niveles rotacionales de energía más bajos, se aproxima bien a una distribución de tipo Boltzmann. Esto nos permite estimar las temperaturas rotacionales, a partir de los espectros de la rama Q ($\nu_1 \sim 3657\text{cm}^{-1}$) y de la simulación de los perfiles de éstos [2]. La evolución temporal de las poblaciones rotacionales se interpretará mediante una Ecuación Maestra que describe la evolución temporal de las poblaciones rotacionales, obteniéndose así las tasas de transferencia colisional inelástica asociadas a cada nivel de rotación a lo largo del jet.

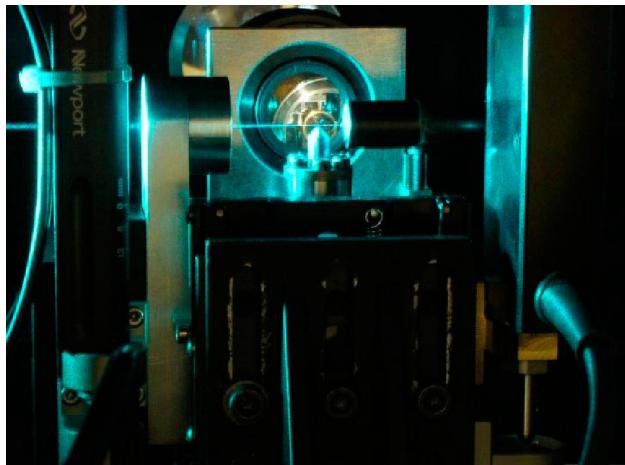


Figura 1: Imagen del interior de la cámara de expansión del sistema experimental (realizada por G. Tejeda).

[1] Tejeda, G.; Maté, B.; Fernández-Sánchez, J.M. y Montero, S. Physical Review Letters, 76, 34-37, (1996).

[2] Avila, G.; Fernández, J. M.; Tejeda, G. y Montero, S. Journal of Molecular Spectroscopy, 228 (1), 38-65, (2004).

Electron and nuclear dynamics of H₂⁺ induced by intense ultrashort laser pulses

R. E. F. Silva¹, F. Catoire², P. Rivière¹, H. Bachau², F. Martín¹

¹Departamento de Química, Universidad Autonoma de Madrid, 28049 Cantoblanco, Madrid, Spain

²CELIA, Université de Bordeaux, France

E-mail: rui.silva@uam.es

We present a theoretical method to extract photoelectron and nuclear kinetic energy spectra of molecules under intense ultrashort laser pulses. The method is applied to H₂⁺ photoionization and dissociation under strong laser pulses with frequencies ranging from extreme- ultraviolet (XUV) to infrared (IR). This method is an extension to molecules of the resolvent technique originally proposed for atoms [1], which was recently implemented to extract absolute values of photoelectron and nuclear kinetic energy spectra [2]. It allows to extract differential probability densities for the different ionization and dissociation channels in the Born-Oppenheimer approximation. In particular, we obtain extremely accurate above-threshold ionization (ATI) spectra. In the case of one-photon absorption (XUV), results show the expected energy sharing between electron and nuclei. For IR we observe ATI, in which there appear two different regimes depending on the electron energy. We propose a mechanism to explain such unexpected behavior.

[1] K. J. Schafer and K. C. Kulander, Phys. Rev. A 42, 5794 (1990)

[2] F. Catoire and H. Bachau. Phys. Rev. A 85, 023422 (2012)

Strong field control of predissociation dynamics

G. Balerdi¹, M.E. Corrales¹, V. Loriot^{1,2}, G. Gitzinger^{1,2}, J. González-Vázquez¹, I. R. Sola¹, R. de Nalda², L. Bañares¹

¹Departamento de Química Física, Facultad de Ciencias Químicas (Unidad Asociada CSIC), Universidad Complutense de Madrid, 28040 Madrid, Spain

²Instituto de Química Física Rocasolano, CSIC, C/ Serrano 116, 28004 Madrid, Spain

E-mail: garikoitz.bv@gmail.com

Strong field control scenarios are investigated in the CH₃I predissociation dynamics at the origin of the second absorption B-band, in which state-selective electronic predissociation occurs through the crossing with a valence dissociative state [1]. Dynamic Stark control (DSC), which was recently demonstrated by Sussman *et. al* [2], and pump-dump strategies are shown capable of altering both the predissociation lifetime of the excited Rydberg state and the product branching ratio.

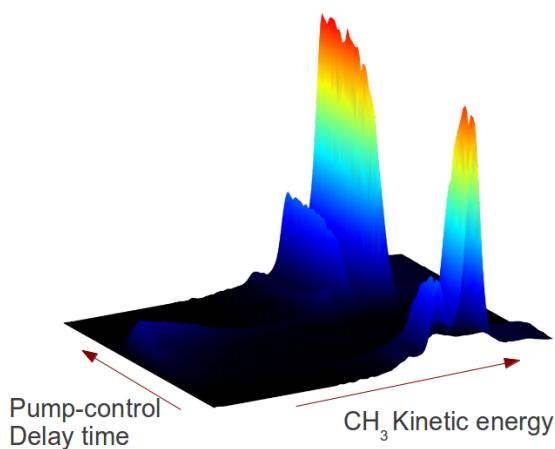


Figure 1. Speed distribution of the CH₃ fragments generated after predissociation of CH₃I as a function of the delay between the pump and control laser pulses. Suppression of the photofragmentation is observed when the pulses are overlapped in time due to dynamic Stark shift (DSS)

[1] G. Gitzinger, M.E. Corrales, V. Loriot, G.A. Amaral, R. de Nalda and L. Bañares, J. Chem. Phys. 132, 234313(2010).

[2] B. J. Sussman, D. Townsend, M. Y. Ivanov and A. Stolow, Science, 314, 278(2006).

Franck-Condon breakdown in k-shell photoionization of small molecules

D. Ayuso¹, K. Ueda², C. Miron³, E. Plésiat¹, L. Argenti¹, M. Patanen³, K. Kooser⁴, S. Mondal², M. Kimura², K. Sakai², O. Travnikova³, A. Palacios¹, P. Decleva⁵, E. Kukk⁴ and F. Martín^{1,6}

¹Departamento de Química, Módulo 13, Universidad Autónoma de Madrid, Cantoblanco
28049 Madrid, Spain

²Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, Senday
980-8577, Japan

³Synchrotron SOLEIL, L'Orme des Merisiers, Saint-Aubin, BP48, 91192 Gif-sur-Yvette
Cedex, France

⁴Department of Physics and Astronomy, University of Turku, FI-20014 Turku, Finland

⁵Dipartimento di Scienze chimiche, Università di Trieste, IT-34127, and CNR-IOM,
Trieste, Italy

⁶Instituto Madrileño de Estudios Avanzados en Nanociencia (IMDEA-Nanociencia),
Cantoblanco, ES-28049 Madrid, Spain

E-mail: david.ayuso@uam.es

The advent of third generation synchrotron radiation sources, in combination with high energy-resolution detection techniques, opened the way to the investigation of vibrationally-resolved inner-shell photoionization in small molecules, such as CH₄, BF₃ or CF₄, in which an electron can be ejected from a 1s orbital of a first-row atom. We theoretically explore these problems by making use of a method based on the static-exchange density functional theory (DFT) [1-3] that includes the nuclear motion. It is well known that shape resonances can give rise to strong deviations from the Franck-Condon (FC) principle near threshold [4] and that multicenter emission from a delocalized molecular orbital can originate Cohen-Fano interferences in photoelectron spectra [5]. Until recently, however, some controversy remained about the origin of the deviations from the FC predictions observed when an electron is ejected from a very localized region in a molecule, such as the 1s orbital of a central atom in a polyatomic molecule [6]. We will show that the ratios between vibrationally resolved photoionization cross sections (v-ratios) exhibit pronounced oscillations at high energies [7], and we will demonstrate that they are due to intramolecular scattering. The latest experiments are in excellent agreement with our first-principles calculations and qualitatively agree with a first-Born approximation model [8,9]. Furthermore, the information carried by the v-ratios is a fingerprint of the molecular geometry and can thus be used to determine structural parameters, such as bond lengths, before and/or immediately after ionization, i.e., for both the neutral molecule and the metastable core-hole species.

- [1] M. Stener, G. Fronzoni and P. Decleva, Chem. Phys. Lett. 351, 469–474 (2002)
- [2] M. Stener and P. Decleva, J. Chem. Phys. 112, 10871 (2000)
- [3] D. Toffoli et al., Chem. Phys. 276, 2543 (2002)
- [4] J. L. Dehmer and Dan Dill, Phys. Rev. Lett. 35, 213–215 (1975)
- [5] S. E. Canton et al., PNAS 108, 7302 (2011).

- [6] E. Kukk, D. Thomas, K. Ueda. J. of Elec. Spectroscopy and Related Phenomena 183 (2011) 53–58
- [7] E. Plésiat et al., Phys. Rev. A 85, 023409 (2012)
- [8] E. Plésiat et al., Phys. Rev. A 85, 023409 (2012)
- [9] L. Argenti et al., New J. Phys. 14, 033012 (2012)

A new way to enhance sensitivity in stimulated Raman spectroscopy: Hollow-core photonic crystal fibers.

Maite Cueto, José Luis Doménech

¹Instituto de Estructura de la Materia (IEM-CSIC), Serrano 123, 28006 Madrid (Spain)

E-mail: maite.cueto@iem.cfmac.csic.es

Stimulated Raman Scattering gain/loss (SRS) processes have a very low efficiency, so, for spectroscopic applications some combination of pulsed laser sources is normally used. Although continuous wave SRS spectroscopy was demonstrated in 1978 by Owyong et al. [1] getting the highest resolution up to now, shortly after that, he developed the quasi-continuous SRS technique which uses a high peak power pulsed pump laser, which is the best compromise achieved between resolution and sensitivity for these gas-phase spectroscopies. A new way to enhance sensitivity without sacrificing resolution, apart from using multipass refocusing cells and cavity enhanced techniques, is to use hollow-core photonic crystal fibers² (HCPCF), which are very suitable due to the tight confinement of light and gas inside the core and the long interaction length. In our set-up for cw-SRS loss spectroscopy, a cw-single mode Ar⁺ probe laser and a cw-single mode tunable dye pump laser (both lasers are stabilized in frequency) interact with a gas sample. Whenever their frequency difference matches that of a Raman-allowed transition of the sample, the probe laser undergoes a loss of power. In our experiment, the gas is placed in a cell formed by a 1.2m length and 4.8μm core diameter HCPCF. We have demonstrated that this new technique enhances the sensitivity of SRS experiments around 6000 times over that of single focus cw-SRS. We will show several examples such as the Q-branch of the ν₁ and 2ν₂ components of the Fermi dyad CO² at 1388 and 1286 cm⁻¹ respectively, or the Q-branch of O² at 1555 cm⁻¹.

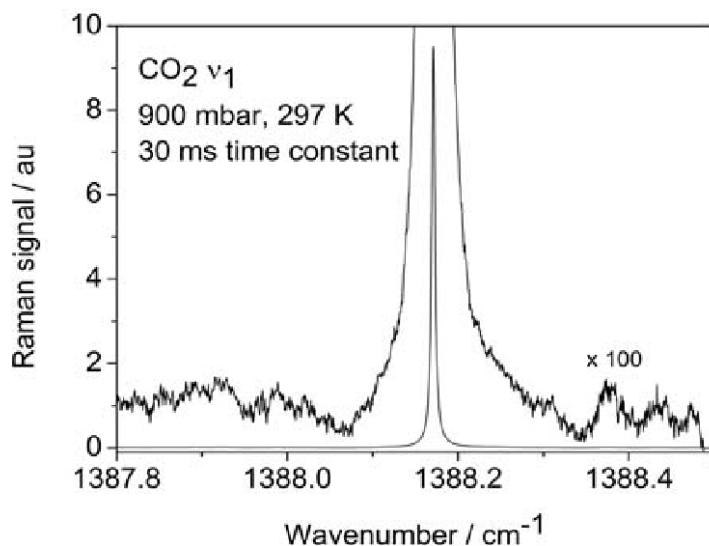


Figure 1: Q-branch of the ν₁ component of the Fermi dyad CO₂ at 1388 cm⁻¹

[1] A. Owyong, C. W. Patterson, R S. McDowell, Chemical Physics Letters, 59, 156-162 (1978)

[2] Philip Russell, et al., Science, 299, 358-362 (2003).

Low-order harmonic generation in nanosecond laser ablation plasmas of carbon containing materials

I. López-Quintás¹, M. Oujja¹, M. Sanz¹, M. Martín¹, R.A. Ganeev², M. Castillejo¹

¹*Instituto de Química Física Rocasolano, CSIC, Serrano 119, 28006 Madrid, Spain*

²*Voronezh State University, Voronezh 394006, Russia*

E-mail: ilopez@iqfr.csic.es

In order to understand and control harmonic generation (HG) processes in laser ablation plasmas [1], knowledge about the species responsible for frequency up-conversion is extremely important. HG emerges as a diagnosis tool to study the nonlinear optical properties of the emitters and in some cases to follow the spatiotemporal behaviour of the species generated in the ablation plume.

In this work, the nonlinear behaviour of laser plasmas produced from carbon containing materials (graphite and boron carbide) was investigated by ablating the targets with a nanosecond Q-switched Nd:YAG laser. The generation of low-harmonics (3rd and 5th) of the fundamental wavelength of a second nanosecond Nd:YAG driving laser, propagating perpendicularly to the ablation beam at a given temporal delay, was observed. Optical emission spectroscopy and time-of-flight-mass spectrometry measurements of the ablation plume revealed details on plasma composition and its spatiotemporal evolution. In particular, in the case of graphite targets, evidence of C₇ up to C₃₂ clusters was found.

In agreement with these findings, deposits collected by on-line pulsed laser deposition showed the presence of carbon based nanoaggregates. This holistic approach to ablation plume analysis allows discussing the identity of the nonlinear emitters in laser ablation plasmas and facilitates the investigation of efficient, nanoparticle-enhanced, coherent short wavelength generation processes.

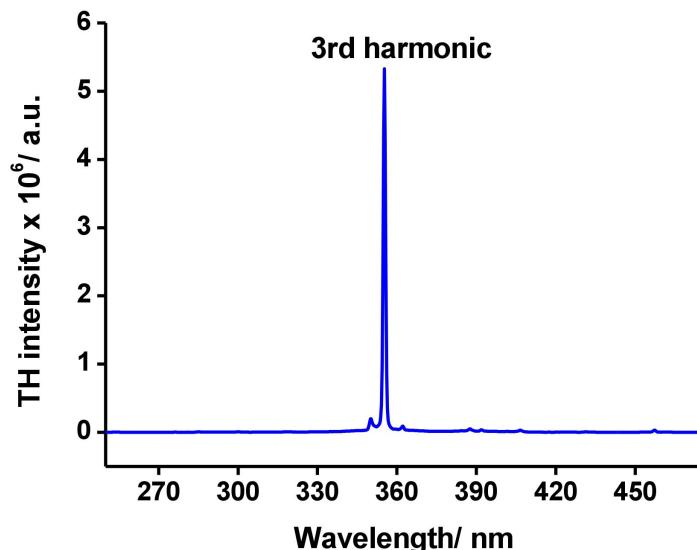


Figure 1: Third harmonic emission at 355 nm observed in graphite ablation plasma.

[1] R.A. Ganeev, J. Phys. B: At. Mol. Opt. Phys., 40, R213-R253 (2007).

Ab initio Force Field for Liquid and Vitreous Silica

Juan J. Nogueira, Yann Danten, Marc Dussauze and Vincent Rodriguez

¹*GSM Institut des Sciences Moléculaires, Université Bordeaux 1, 351, Cours de la Libération 33405 Talence Cedex, France*
E-mail: juanjonog@hotmail.com

Silica is probably one of the most studied materials by both theoretical simulations and experimental techniques because of its relevance in many fields, including materials science, electronics and geophysics. It is a key material in many technological and industrial sectors such as optical fibers, semiconductor devices and glass manufacturing. In addition, beyond its technological applications, liquid ($l\text{-SiO}_2$) and vitreous ($v\text{-SiO}_2$) phases of silica are also considered the archetype of the tetrahedral liquids [1] and the disordered network glasses [2] respectively.

A complete understanding of the physical properties of $l\text{-SiO}_2$ and $v\text{-SiO}_2$ is a great challenge since the lack of long-range order makes the interpretation of many experimental measurements very difficult, or at least ambiguous. Therefore, atomistic simulations have become a valuable tool for investigating the features of these disordered materials. In this work, we have developed an analytical potential energy surface, based on high-level ab initio calculations, to study the structure and the spectroscopic activity of silica by molecular dynamics simulations. The first results show a good description of both short-range and medium-range structure of the material in comparison with experimental diffraction data.

[1] Shadrack Jubes, B.; Nayar, D.; Dhabal, D.; Molinero, V.; Chakravarty, C. *Journal of Physics Condensed Matter* 24, 284116-284126 (2012).

[2] Kob, W. *Journal of Physics Condensed Matter* 11, R85-R115 (1999).

Ion-Molecule Reactions with alkali metals

E.López¹, J.M.Lucas¹, J. de Andrés¹, M. Albertí¹, A. Aguilar¹
¹University of barcelona
E-mail: estefania.lopez.marne@gmail.com

Collisions between ions and neutral molecules are very important in scientific studies, and we can find them in the study of atmospheric processes, gas-phase catalysis or different types of plasmas [1]. In the last years GQRD group study has been focused in excitation and charge transfer processes in several systems composed of alkaline ions and neutral molecules. There are three possible processes that can be studied: Formation of clusters or adducts between alkaline ions (Li^+ , Na^+ , K^+) and neutral molecules (i-bromopropane, benzene...), Charge transfer processes among the alkali ion and the gas molecule (N_2 , CO_2), and Fragmentation reactions. To carry out the reactions our group use crossed molecular beams techniques, and studies the different fragments formed in the collision by a quadrupolar mass analyser.

In these work we present the system formed by neutral molecules of isobromopropane and Li^+ , Na^+ and K^+ ions, measuring the Experimental Cross Sections by an apparatus [2] designed and built in our group and calculating the Potential Energy Surfaces by ab-initio calculations.

The next step will be to carry out Dinamical Trajectories “on the fly”.

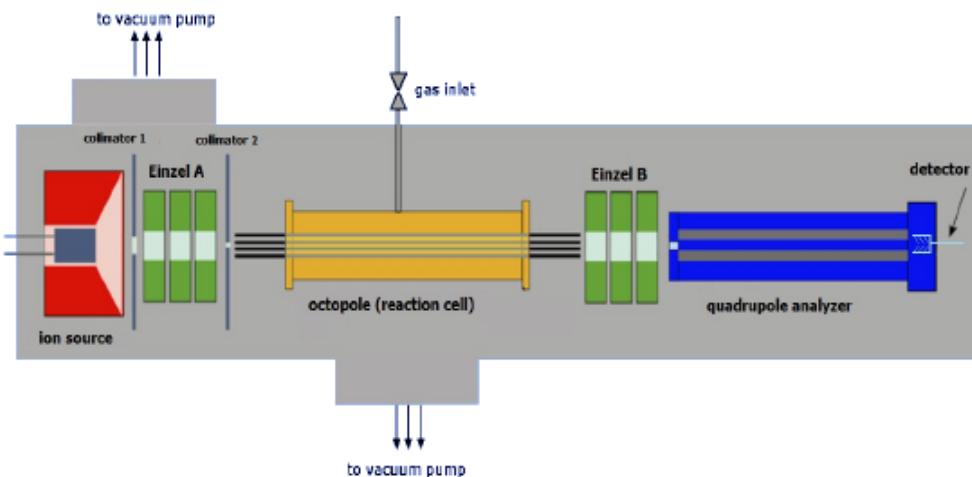


Figure 1: Apparatus diagram

- [1] M. Sabidó, J. de Andrés, J. Sogas, J.M. Lucas, M. Albertí, J.M. Bofill, I. Rabadán, A. Aguilar, The European Physical Journal D, 47 (2008) 63-70.
- [2] M.Sabidó, J.M.Lucas, J. de Andrés, J.Sogas, M. Albertí, A.Aguilar, D. Bassi, D. Ascenzi, P. Franceschi, P. Tosi, F. Pirani, Chemical Physics Letters 442 (2007) 28-34.

Optimal covering of C_{60} fullerene by rare gases

S. Acosta-Gutiérrez

¹Departamento de Física Fundamental II, Universidad de La Laguna, E-30205 La Laguna, Tenrife, Spain

E-mail: silviaa.gutierrez@gmail.com

Putative global energy minima of clusters formed by the adsorption of rare gases on a C_{60} fullerene molecule, $C_{60} X_N$ ($X=Ne, Ar, Kr, Xe; N \leq 70$), are found using basin-hopping global optimization in an empirical potential energy surface. The association energies per rare gas atom as a function of N present two noticeable minima for Ne and Ar and just one for Kr and Xe. The minimum with the smallest N is the deepest one and corresponds to an optimal packing monolayer structure; the other one gives a monolayer with maximum packing. For Kr and Xe optimal and maximum packing structures coincide. By using an isotropic average form of the $X-C_{60}$ interaction, we have established the relevance of the C_{60} surface corrugation on the cluster structures. Quantum effects are relevant for Ne clusters. The adsorption of these rare gases on C_{60} follows patterns that differ significantly from the ones found recently for He by means of experimental and theoretical methods.

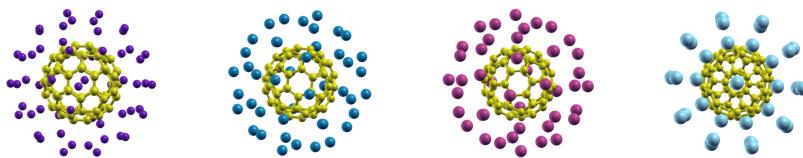


Figure 1: Geometrical structure of global minima for $C_{60} X_N$ ($N= Ne, Ar, Kr, Xe$)

[1] S. Acosta-Gutiérrez, J. Bretón, J.M. Gómez Llorente and J. Hernández-Rojas, J. Chem. Phys. 137, 074306 (2012).

Theoretical treatment of the fragmentation dynamics of excited highly charged fullerenes

H. Jr. Silva¹, S. Díaz-Tendero¹, P.A. Hervieux², M. Alcamí¹, and F. Martín^{1,3}

¹Departamento de Química, Universidad Autónoma de Madrid, 28049 Madrid (Spain).

²Institut de Physique et Chimie des Matériaux de Strasbourg, UMR 7504,

CNRS-Université de Strasbourg, 67034 Strasbourg (France).

³Instituto Madrileño de Estudios Avanzados en Nanociencia (IMDEA-Nanociencia), 28049 Madrid (Spain).

E-mail: humberto.silva@uam.es

Carbon cluster fragmentation induced by previous excitation processes has been used as a tool to understand structure and stability of fullerenes. Indeed, collisions of highly charged ions with C₆₀ have been intensively studied for more than one decade (see e.g. [1]). In these collisions, several C₆₀ electrons may be ionized and transferred to the charged projectile, thus leading to the formation of excited multiply charged C_{60^{q+}} fullerenes. In general, ionization and excitation processes in a collision are much faster than fragmentation. Thus fragmentation can be studied separately and the physical quantity that links both processes is the excitation energy deposited in the collision. Different competitive processes may take place after the collision to cool down the cluster such as photon, electron, and neutral or charged fragments emissions. Since fragmentation is a common escape door for charged fullerenes excited above their stability threshold [1], the study of the dominant decay channels is used to obtain qualitative information on the cluster structure and stability. In the case of C₆₀, experiments have shown that the main de-excitation pathway is the emission of one or several C₂ or C₂⁺ fragments [2]. Since excited and highly charged fullerenes show a great stability even in extreme conditions, it allows measuring these species in the experimental “time-windows”.

From the theoretical point of view, the standard method used to study post-collisional fragmentation processes of excited clusters is molecular dynamics (MD) simulations. Due to the large number of degrees of freedom shown by the fullerene, its high stability and the large amount of time needed to undergo fragmentation, MD simulations incorporating any quantum mechanics level of approximation leads to extremely high computational cost simulations. Alternatively in this work we describe fullerene fragmentation using the Weisskopf theory [3], a first order time-dependent perturbation - and statistical – theory, which is computationally much cheaper than MD methods. The Weisskopf formalism has been applied successfully to description of fragmentation of metal clusters [4] and small carbon clusters [5]. Using this method implies that (i) we have an analytical solution of the equations that describe the fragmentation rate constant decreasing enormously the computational cost; (ii) it is a method based in the Fermi’s golden rule (first order time-dependent perturbation theory) which means a quantum mechanics based treatment of the time-dependence required by our problem; and (iii) we use the statistical mechanics for the description of the density of states of the excited species. In this work all the information needed to implement the method (geometries, frequencies, energies, etc.) was computed at DFT/B3LYP level of theory, since it has been proved to be a good choice for carbon clusters: the obtained results are in reasonable agreement with MP2 and CCSD(T) calculations and, also, with experimental measurements [6].

In this communication [8] we will present the theoretical results obtained for the fragmentation dynamics of excited C₆₀. In particular, competition between C₂ and C₂⁺ evaporation

as a function of the initial charge of the fullerene, the excitation energy and the time after the excitation. Furthermore, we will compare our results with recent experimental measurements [7].

- [1] E. E. B. Campbell and F. Rohmund Rep. Prog. Phys. 2000, 63, 1061.
- [2] H. Cederquist et al., Phys. Rev. A 2003, 67, 062719.
- [3] V. Weisskopf. Phys. Rev. 1937 52, 295.
- [4] B. Zarour, J. Hanssen, P.-A. Hervieux, M. F. Politis, and F. Martin. J. Phys. B. 2000 33, L707.
- [5] G. Martinet, S. Díaz-Tendero, M. Chabot et al. Phys. Rev. Lett. 2004 93, 063401.
- [6] S. Díaz-Tendero, M. Alcamí and F. Martín, J. Chem. Phys, 2003 119, 5545.
- [7] P. Rousseau and H. Zettergren, private communication.
- [8] H. Jr. Silva et al. in preparation

Density Functional Theory study on the interaction between Metals and C₆₀

M. Robledo¹, author² S. Díaz-Tendero¹, F. Martín^{1,2} and M Alcami²

¹Departamento de Química Módulo 13, Universidad Autónoma de Madrid, 28049-Madrid, Spain

²Instituto Madrileño de Estudios Avanzados en Nanociencia (IMDEA-Nanociencia), Cantoblanco, 28049 Madrid, Spain

E-mail: maitreyi.robledo@uam.es

The discovery of C₆₀ (Fullerene)[1], and other related carbon nanostructures, has meant the landmark of intense investigation devoted to the possibility of giving these systems new physical and chemical properties, useful in the fields of nanotechnology, molecular electronics, photovoltaic applications, etc. Fullerides[2], molecular solids built by the arrangement of C₆₀ in a close packing structure as K₃C₆₀, base their stability on the charge transfer between the species constituting the solid. Motivated by these features, previous works (see e.g. [3,4,5] and references therein) have studied the possibility of doping a single C₆₀ molecule, instead of the whole solid. However, these former studies considered only a few metal atoms, mainly alkaline metals. This fact motivated us to carry out a thoroughly and systematic study in which different metals are considered in the interaction with the fullerene. This has brought us the possibility of finding common trends for metals belonging to the same group of the Periodic Table and similar behaviors between all metals, regardless the group. Within this main purpose, we have performed a systematic theoretical study on the exohedral interaction between singly charged metal atoms and the C₆₀ fullerene, MC₆₀⁺, where M is an alkaline, alkaline-earth or a first row transition metal. The calculations have been performed in the framework of Density Functional Theory. In particular, we have used the hybrid B3LYP functional in combination with the 6-31G(d) basis set. We have considered in our calculations five types of initial geometries with the metal atom interacting with the fullerene external surface: hexagonal (h) and pentagonal (p) rings, the double (hh) and single (hp) bonds and on top of a carbon atom (C). We have evaluated the type of interaction by studying relative energies, electronic and structural features of the different encountered isomers. In this communication we will report on the binding energies and on the nature of the interaction, which can be explained with a simple ion-induced dipole electrostatic model.

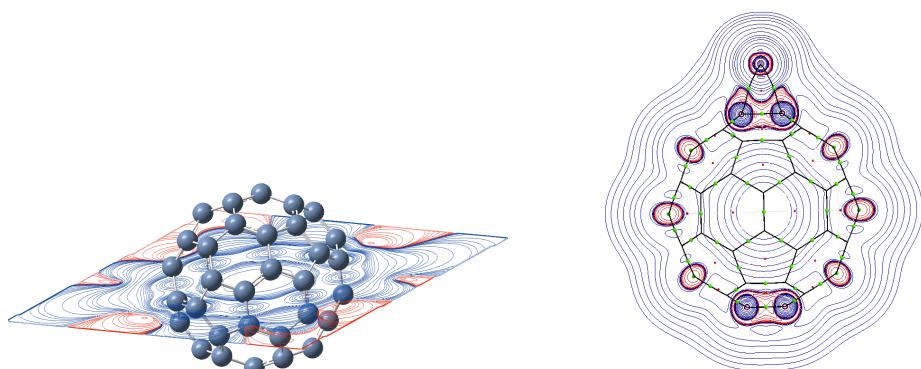


Figure 1: Molecular Electrostatic Potential (MEP) map for C₆₀ on the left and Bader's Atoms in Molecules contour for FeC₆₀⁺ on the right. Both of them bring forward the ion-induced dipole electrostatic model.

[1] H. W. Kroto, J. R. Heath, S. C. O'Brien, R. F. Curl, R. E. Smalley, Nature, 1985, 318, 162-163

- [2] W. Kramer, L.D. Lamb, K. Fostiropoulos, D.R Hoffman, Nature, 1990, 347, 354-358
- [3] F. Rabilloud, J. Phys. Chem. A, 2010, 114, 7241-7247
- [4] T.P Martin, N. Malinowski, U. Zimmermann, U. Näher, H. Shaber, J. Chem. Phys., 1993, 99, 4210
- [5] J. Kohanoff, W. Andreoni, M. Parrinello, Chem. Phys. Lett., 1992, 198, 472

Study of Ca impurity in helium clusters

R. Rodríguez-Cantano¹, D. López-Durán¹, T. González-Lezana¹, F. A. Gianturco², G. Delgado-Barrio¹, and P. Villarreal¹

¹*Institute of Fundamental Physics, IFF-CSIC, Madrid, Spain*

²*Department of Chemistry and CNISM, University of Rome La Sapienza, Italy*

E-mail: rrcantano@iff.csic.es

Following recent works [1-3], we present path integral Monte Carlo (PIMC) calculations [4] for the structure and energetics of ${}^4\text{He}_N$ nanodroplets doped with a single calcium atom. Sizes ranging from 10 and 40 helium atoms were considered at temperatures of 1, 1.5 and 2 K. Simulations have been carried out using two different He-Ca interactions, Kleinekathöfer [5] and Lovallo [6], which reveal substantial discrepancies regarding the precise location of the Ca impurity with respect to the helium droplet and the total energy of the system. The different nature of the He-Ca and He-He interactions has been found to be crucial to understand the marked differences between the PIMC predictions in its classical and quantum mechanical versions.

- [1] D. Mateo, M. Barranco, R. Mayol, M. Pi, Eur.Phys. J. D. 52, 63-66 (2009)
- [2] A. Hernando et al., J. Phys. Chem. A. 111, 7303-7308 (2007)
- [3] D. López-Durán et al., Phys. Rev. A. 86, 022501 (2012)
- [4] D. M. Ceperley, Rev. Mod. Phys. 67, 279 (1995).
- [5] U. Kleinekathöfer, Chem. Phys. Lett. 324, 403-410 (2000)
- [6] C. C. Lovallo, M. Klobukowski, J. Chem. Phys. 120, 246 (2004)

Ultrafast Photophysics of Simple Aromatic Chromophores

Virginia Ovejas¹, Raúl Montero¹, Álvaro Peralta Conde², Marta Fernández-Fernández¹, and Asier Longarte¹

¹Departamento de Química Física. Universidad del País Vasco (UPV/EHU). Apart. 644, 48080 Bilbao, Spain

²Centro de Láseres Pulsados (CLPU), Edificio M3, Parque Científico, 37185 Villamayor, Spain.

E-mail: virginia.ovejas@ehu.es

Although aromatic Chromophores as Indole, Phenol, Aniline, Pyrrole and others are characterized by having bright $\pi\pi^*$ electronic transitions, often their photophysical properties are strongly dependent on the interaction of these $\pi\pi^*$ excitations with $\pi\sigma^*$ type states with repulsive character along some vibrational coordinates. The interplay between these two types of states triggers a complex dynamics that takes place in the femto-picoseconds scale [1].

Our group is interested in understanding the ultrafast relaxation mechanisms involving $\pi\sigma^*$ surfaces in a set of isolated aromatic chromophores, which are present in molecules of biological interest as aminoacids or nucleobases. In the carried out research, the dynamical signature of the $\pi\sigma^*$ states has been tracked directly on the parent molecules photoexcited in a broad range of their near UV absorption spectra, by multiphoton delayed ionization at several wavelengths. These femtosecond resolution experiments with parent ion detection, achieve the required sensitivity to simultaneously measure major and minor relaxation channels, providing a general view of the photophysics of the systems [2,3,4].

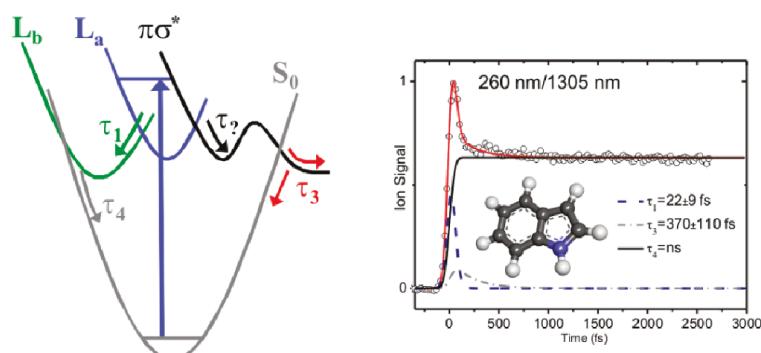


Figure 1: Cartoon of the relaxation processes observed for the indole molecule following excitation in the 263–243 nm interval. τ_1 , τ_3 , and τ_4 are the lifetimes extracted from the transients collected.

[1] Wolfgang Domcke, et al. Science 302, 1693 (2003).

[2] R. Montero et al J. Chem. Phys. 135, 054308 (2011).

[3] R. Montero et al J. Phys Chem.A. 116(11):2698-703 (2012).

[4] Asier Longarte, et al J. Chem. Phys. 137, 064317 (2012).

Femtosecond ultrafast evolution of Imidazole and Pyrrole after electronic excitation

Marta Fernández-Fernández¹, Raúl Montero¹, Virginia Ovejas¹, Álvaro Peralta Conde², and Asier Longarte¹

¹Departamento de Química Física. Universidad del País Vasco (UPV/EHU). Apart. 644, 48080 Bilbao, Spain

²Centro de Láseres Pulsados (CLPU), Edificio M3, Parque Científico, 37185 Villamayor, Spain.

E-mail: martafernandez051@ikasle.ehu.es

Pyrrole and Imidazole are heteroatomic aromatic molecules with relevant chromophoric properties in biology. Imidazole is a subunit of the purine nucleobases and the chromophore of some significant compounds, as the amino acid histidine or the pigment urocanic acid. On the other hand, substituted pyrroles are the constituent units of porphyrins based pigments and other relevant compounds, being also closely related to the pyrimidinic DNA bases.

The complex photophysical behavior of these molecules is determined by the repulsive $\pi\sigma^*$ character of their lowest energy electronic excitations, which strongly interacts with the bright $\pi\pi^*$ transitions characteristic of the chromophores. Time resolved studies with ultrafast resolution were carried out in the 265-217 nm excitation interval, allowing us to track the dynamical processes induced by the presence of the $\pi\sigma^*$ states. Two ultrashort lifetimes, which are associated with the IC from the bright ${}^1\text{B}_2 \pi\pi^*$ state, and the propagation of the wavepacket on the $\pi\sigma^*$ state, respectively, are extracted from the time dependent signals. The works also explores the consequences of the adiabatic excitation of the system when broadband femtosecond pulses are employed to prepare the molecule in the targeted electronic states, revealing the key implication of this type of coherent phenomena. The collected data reveal that the bright ${}^1\text{B}_2 \pi\pi^*$ state is adiabatically populated at excitation wavelengths far away from resonance, providing an efficient way to reach the $\pi\sigma^*$ state. The recorded transients are fit employing a coherent model that provides a comprehensive view of the dynamical processes these molecules undergoes after excitation by ultrashort light pulses.

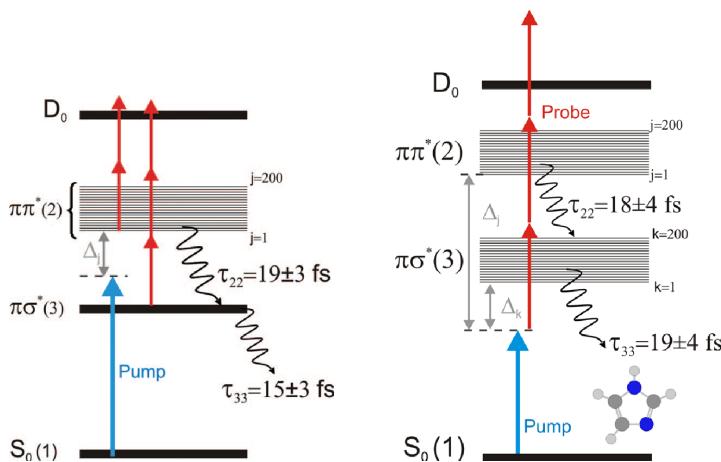


Figure 1. Schemes of the electronic states and processes considered to model the observed pyrrole (A) and imidazole (B) dynamics.

[1] R. Montero et al, J. Chem. Phys, 137, 064317 (2012)

[2] R. Montero et al, J. Phys. Chem. A, 116, 10752–10758 (2012)

Rotational Spectra of Sugars: Ribose and Fructose

P. Écija¹, E.J. Cocinero¹, A. Lesarri², A. Cimas³, B.G. Davis⁴, F.J. Basterretxea¹, J.-U. Grabow⁵, J.A. Fernandez¹, and F. Castaño¹

¹Departamento Química Física, Facultad de Ciencia y Tecnología, Universidad del País Vasco (UPV-EHU), Apartado 644, 48080 Bilbao (Spain)

²Departamento de Química Física y Química Inorgánica, Facultad de Ciencias, Universidad de Valladolid, 47011 Valladolid (Spain)

³Centro de Investigação em Química, Faculdade de Ciências, Universidade do Porto, 4169-007 Porto (Portugal).

⁴Chemistry Department, Oxford University, Chemistry Research Laboratory, 12 Mansfield Road, OX1 3TA Oxford (United Kingdom)

⁵Institut für Physikalische Chemie und Elektrochemie, Gottfried-Wilhelm-Leibniz Universität Hannover, Callinstraße 3A, 30167 Hannover (Germany)

E-mail: patricia.ecija@ehu.es

Sugars are aldoses or ketoses with multiple hydroxy groups which have been elusive to spectroscopic studies. Here we report a rotational study of the aldopentose ribose and hexoketose fructose.

The aldoses and hexoses can exhibit alternative linear or cyclic forms, closing either five-membered (furanose) or six-membered (pyranose) rings. In both rings α and β anomers are possible depending on the orientation of the hydroxy group at anomeric carbon. The furanose form is predominant in biochemical relevant molecules such as ribonucleosides RNA, or in sucrose; but is furanose the native form of free ribose and/or fructose? Recent condensend-phase X-ray [1] and older NMR [2] studies delivered conflicting results.

In order to solve this question we conducted a microwave study on ribose and fructose that, owing to ultrafast UV laser vaporization [3], have become the first C-5 (ribose) and C-6 (fructose) sugars observed with rotational resolution. The spectrum of D-ribose revealed six conformations, preferentially adopting β -pyranose chairs as well as higher-energy α -pyranose forms. The method also allowed for unambiguous distinction between different orientations of the hydroxy groups, which stabilize the structures by cooperative hydrogen-bond networks.

In the case of fructose, the rotational spectrum for the parent, all monosubstituted ^{13}C species and two single D species reveals unambiguously that the free hexoketose is conformationally locked in a single dominant β -pyranose structure. The structure of free fructose has been determined experimentally using substitution and effective structures. The experimental work was supported by ab initio and DFT calculations.

[1] a) Sisak, D.; McCusker, L. B.; Zandomeneghi, G.; Meier, B. H.; Bläser, D.; Boese, R.; Schweizer, W. B.; Gylmour, R.; and Dunitz J. D. *Angew. Chem. Int. Ed.*, 49, 4503 (2010). b) Saenger, W. *Angew. Chem. Int. Ed.*, 49, 6487 (2010).

[2] a) Rudrum, M.; and Shaw, D. F. *J. Chem. Soc.*, 52 (1965). b) Lemieux, R. U.; and Stevens, J. D. *Can. J. Chem.*, 44, 249 (1966). c) Breitmaier, E.; and Hollstein, U. *Org. Magn. Reson.*, 8, 573 (1976).

[3] Cocinero, E. J.; Lesarri, A.; Ecija, P.; Basterretxea, F. J.; Grabow, J-U.; Fernández, J. A.; and Castaño, F. *Angew. Chem. Int. Ed.*, 51, 3119 (2012).

**Espectroscopía electrónica con resolución de masas de
 β -Fenil-D-Glucopiranosa-D-Glucosa en expansiones supersónicas**
Imanol Usabiaga¹; Pedro F. Arnaiz¹; Jorge González¹; Judith Millán²; Iker León¹; Emilio J. Cocinero¹, José A. Fernández¹.

¹ Universidad del País Vasco UPV/EHU

² Universidad de La Rioja

E-mail: usabiagakie@hotmail.com

Entre las distintas técnicas espectroscópicas la espectroscopía laser con resolución de masas permite obtener información de los complejos moleculares, escogiendo el número de ligandos y distinguir la espectroscopía de cada uno de ellos por separado. La combinación de esta técnica con métodos de preparación de muestra, como la expansión supersónica y la ablación laser permiten, por una parte, obtener espectros de los isómeros más estable simplificando mucho su interpretación, y por otro lado, el estudio de moléculas térmicamente inestables en fase gas. Las reacciones biológicas se caracterizan por una gran especificidad, debida al reconocimiento molecular que se da entre las distintas moléculas participantes en el proceso. El anclaje tiene lugar a través de la formación de complejos o agregados moleculares, que pueden estudiarse mediante la combinación de espectroscopía electrónica con resolución de masas y expansiones supersónicas. Algunos de los sistemas que se estudian guardan relación con procesos de reconocimiento molecular asociados al anestésico propofol [1] e interacciones de azúcares relacionado con el proceso de anclaje que tiene lugar en las glicoproteínas de la membrana celular [2].

En esta comunicación se presentarán los resultados del estudio de la β -Fenil-D-Glucosa y sus complejos con D-Glucosa empleando una combinación de espectroscopía electrónica con resolución de masas y cálculos mecano-cuánticos. Mediante el empleo de ablación láser es posible pasar el azúcar a fase gas y mediante una expansión supersónica es subsecuentemente enfriado, formando además agregados moleculares. El empleo de diversas técnicas espectroscópicas permite la obtención de espectros electrónicos e IR del complejo, cuya comparación con las predicciones para las estructuras calculadas (Figura 1) empleando métodos DFT, permite la asignación de los isómeros encontrados experimentalmente.

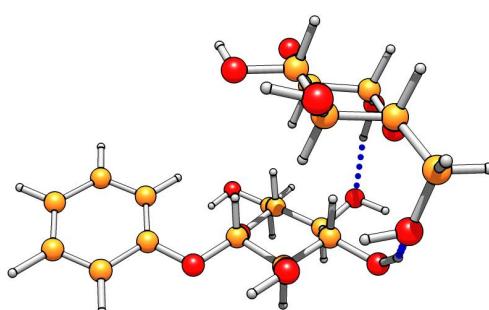


Figura 1; Estructura de uno de los mínimos de energía del complejo formado por β -Fenil-D-Glucopiranosa con D-Glucosa.

[1] Iker Leon, Judith Millán, Emilio J. Cocinero, Alberto Lesarri, Fernando Castaño and José A. Fernández, Phys. Chem. Chem. Phys. 14, 8956-8963, 2012.

[2] Cocinero, Emilio J.; Carcabal, Pierre; Vaden, Timothy D.; NATURE; 469; 7328; 76-U1400

Structure of Succinic Acid in the gas phase

Estíbaliz Méndez, Lorena Miñambres, Patricia Écija, Emilio Cociñero, F. Castaño and Francisco J. Basterretxea

¹ Universidad del País Vasco, Barrio Sarriena (UPV/EHU) s/n, 48940, Leioa
E-mail: estibaliz.mendez@ehu.es

Atmospheric aerosols are microscopic particles suspended in the Earth's atmosphere and are a major environmental agent. They affect visibility, human health and influence climate by absorbing and reflecting solar radiation and modifying cloud formation. It is not fully understood at molecular level how aerosols form, creating one of the largest sources of uncertainty in atmospheric models and climate prediction[1]. The chemical formation of aerosols is known as nucleation, in which gaseous molecules bond together. It is suggested that one H₂SO₄ or NH₃ molecule and one organic molecule are involved in the rate limiting step of the nucleation process in the Earth's troposphere[2]. It is thought that this organic molecule is a dicarboxylic acid because in one extreme it is strong hydrogen-bonded to H₂SO₄/ NH₃ and the free carboxylic group allows the growth of the complex until the aerosol is formed[3]. To get a better understanding of the nucleation process, it is necessary to know the chemical structure of the molecules implicated like succinic acid. This dicarboxylic acid was vaporized by UV ultrafast laser ablation[4] and diluted into an expanding stream of Ne forming a supersonic jet, where the molecules were probed by time-domain rotational spectroscopy. The most stable conformer was characterized in the rotational spectrum. All monosubstituted isotopic species (¹³C, ¹⁸O, ²H) were positively identified leading to an accurate determination of the effective and substitution structures of the molecule. Ab initio (MP2) and DFT (M062X and B3LYP) calculations supplemented the experimental work.

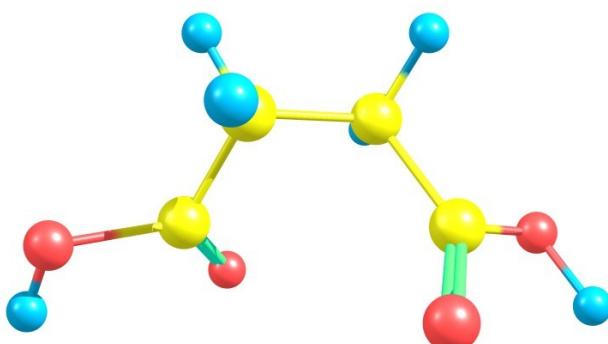


Figure 1: Structure of succinic gas phase

- [1] Zhang, R., Science, 328, 1366-1367 (2010).
- [2] Axel Metzger, Bart Verheggen, Josef Dommen, Jonathan Duplissy, Andre S. H. Prevot, Ernest Weingartner, Ilona Riipinen, Markku Kulmala, Dominick V. Spracklen, Kenneth S. Carslaw, and Urs Baltensperger , Proc. Natl. Acad. Sci., 107, 6646 - 6651, (2009).
- [3] Wen Xu and Renyi Zhang, The Journal of Physical Chemistry A, 116, 4539 – 4550, (2012).
- [4] Emilio J. Cociñero, Alberto Lesarri, Patricia Écija, Francisco J. Basterretxea, Jens-Uwe Grabow, José A. Fernandez, and Fernando Castaño, Angewandte Chem. Int. Ed., 51, 3119 – 3124, (2012).

Clustering en experimentos de imagen mediante cadenas de Markov (RankCompete)

Roberto Fernández¹, Egoitz Astigarraga², Jose A. Fernández¹

¹ Grupo de espectroscopía y espectrometría de masas, departamento de química Física, Facultad de ciencia y tecnología, Universidad del país vasco, Barrio Sarriena s/n, 48940 Leioa, España.

² IMG Pharma Biotech S.L. Leioa, España. Vivero de Empresas (ZITEK Mintegia). Módulo 7 UPV/EHU. Edificio de rectorado, Barrio Sarriena s/n 48940-Leioa (Spain)
E-mail: Robertoantonio.fernandez@ehu.es

En la actualidad, numerosas técnicas, tanto en el campo de la espectroscopía como de la espectrometría de masas, son capaces de obtener resultados con resolución espacial. Esto es debido, en parte, a la gran capacidad de los ordenadores modernos que permite trabajar con la ingente cantidad de datos que este tipo de experimentos de Imagen (Imaging) genera. En estos momentos ya se están empleando diversas técnicas de análisis que permiten diferenciar áreas de interés en las muestras en función de la similitud de sus espectros como el análisis por componentes principales (PCA) o el clustering K-means. Sin embargo, dichos algoritmos tienen problemas para identificar todas las áreas en experimentos con un gran número de variables, debido a las limitaciones de los métodos lineales de análisis. Por este motivo es interesante la implementación de nuevos algoritmos que permitan mejorar o fortalecer este campo. En este trabajo, se emplea el concepto de las cadenas de Markov, en concreto el caso particular conocido como paseo aleatorio o Random Walk (RW), asignando una probabilidad de salto basada en la similitud de los estados [1] y haciendo competir dos o más paseos aleatorios, entre sí, por toda el área del experimento (RankCompete)[2], para obtener dos o más regiones de interés diferenciadas por el comportamiento de las variables asignadas. Para comprobar el éxito del método se han empleado, primero un sistema sencillo pregenerado y posteriormente un experimento en (MALDI-IMS) sobre una placa de TLC (Thin layer chromatography) en la que se han depositado varios patrones de lípidos.



[1] Lawrence Page, “Method for node ranking in a linked database”, United States Patent, Sep. 4, 2001, Patent No.: US 6,285,999 B1.

[2] Liangliang Cao, Andrey Del Pozo, Xin Jin, Jiebo Luo, Jiawei Han and Thomas S. Huang, “RankCompete: Simultaneous ranking and clustering of web photos”, WWW 2010, ISBN: 978-1-60558-799-8 DOI 10.1145/1772690.1772809.

Theoretical study of the reaction of S⁺ with vibrationally excited H₂

A. Zanchet¹, O. Roncero², A. Aguado³ and M. Agúndez⁴

¹*Instituto de Estructura de la materia, C.S.I.C., Serrano 123, 28006 Madrid, España.*

²*Instituto de Física Fundamental , C.S.I.C., Serrano 123, 28006 Madrid, España.*

³*Departamento de Química Física, Facultad de Ciencias C-XIV,
Universidad Autónoma de Madrid, 28049 Madrid, España.*

⁴*Laboratoire d'Astrophysique de Bordeaux, Observatoire Aquitaine des Sciences de l'Univers,
Université Bordeaux 1, 2 rue de l'Observatoire, BP 89, 33271 FLOIRAC CEDEX, France.*

E-mail: zanchet@iem.cfmac.csic.es

The SH⁺ molecule has been recently observed in interstellar medium, although its mechanism of formation is still not clear. One of the possible reaction leading to this molecule is the collision of the sulfure ion with H₂, the most abundant molecule in interstellar medium. The reactions S⁺+H₂ → SH⁺+H is endothermic by 0.86 eV and, therefore, is expected to have small rate constant at low temperature. Nevertheless, recent studies indicate that vibrationally excited H₂, which can be encountered in dense photon dominated regions, may favour this reaction and make it the main source of SH⁺ in such interstellar regions [1].

In this work, we will present the reaction dynamics study of the title reaction, taking in account the vibrational excitation of the H₂ molecule. The calculations were done using quantum and quasi-classical dynamics methods using an accurate potential energy surface we built based on *ab initio* electronic structure calculations. The cross sections and rate constants were calculated for several vibrational level of H₂ to check the effect of vibration of H₂ and how it enhance the reactivity of this system.

[1] M. Agúndez et al., Ap. J. **713**, 662 (2010).

Charge-exchange and ionization cross sections for atomic collisions relevant in fusion research

A. Jorge, L.F. Errea, C. Illescas, and L. Méndez

¹*Laboratorio de Física Atómica y Molecular en Plasmas de Fusión asociado al CIEMAT Departamento de Química, Módulo 13, Universidad Autónoma de Madrid Cantoblanco, 28049 Madrid, SPAIN*
E-mail: alba.jorge@uam.es

We have calculated ionization and charge-exchange cross sections for C^{6+} , $N^{7+} + H(n = 1, 2)$ collisions in the energy range $10 < E < 500$ keV/amu. These results are needed for Charge eXchange Recombination Spectroscopy (CXRS) diagnostic in fusion plasma research [1]. We have employed the Classical Trajectory Monte Carlo (CTMC) method, which provides reliable total as well as n and nl-resolved cross sections for charge-exchange in the mentioned energy range. A complete description of this method can be found in [2]. We have implemented two different initial distributions in order to describe the target H atom, the so-called microcanonical and hydrogenic distributions.

Our results for $A^{q+} + H(1s)$ collisions agree well with very recent AOCC data [3] and experiments [4,5]. We also find reasonable agreement with AOCC results in the case of collisions with the ex-cited target H($n=2$), where the microcanonical and hydrogenic distributions lead to similar results.

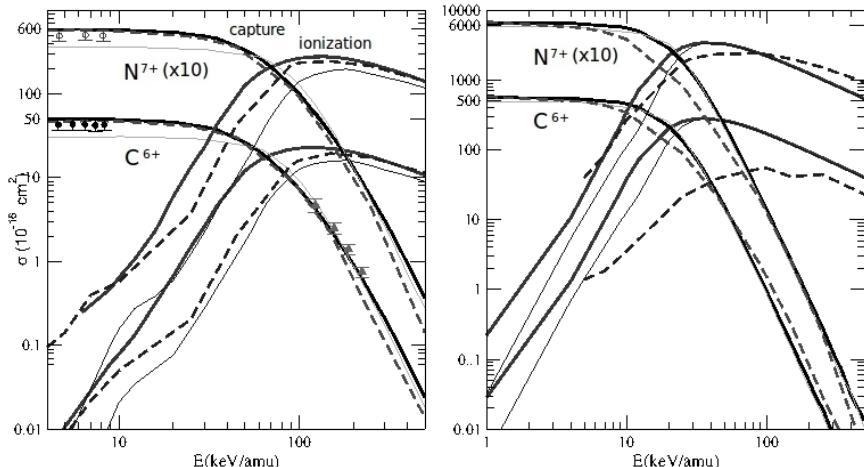


Figure 1: Total ionization and electron capture cross sections for C^{6+} , N^{7+} colliding with $H(1s)$ (left), and $H(n=2)$ (right). Data presented: hydrogenic (thick solid line) and microcanonical (thin solid line) distribution; AOCC (dashed line) [3]; experimental: (filled triangles) [4]; (filled circles) [5]

[1] www.adas-fusion.eu

[2] L. F. Errea et al. Phys. Rev. A 70, 052713 (2004)

[3] K. Igenbergs et al., J. Phys. B 45, 065203 (2012).

[4] T. V. Goffe et al. J. Phys. B 12, 3763 (1979).

[5] F. W. Meyer et al. Phys. Rev. A 32, 3310 (1985).

Full-dimensional ab initio potential energy surface and dynamics for the H_7^+ cluster

P. Barragán¹, R. Pérez de Tudela², R. Prosmitti¹, Y. Wang³, C. Qu³, and J. M. Bowman³

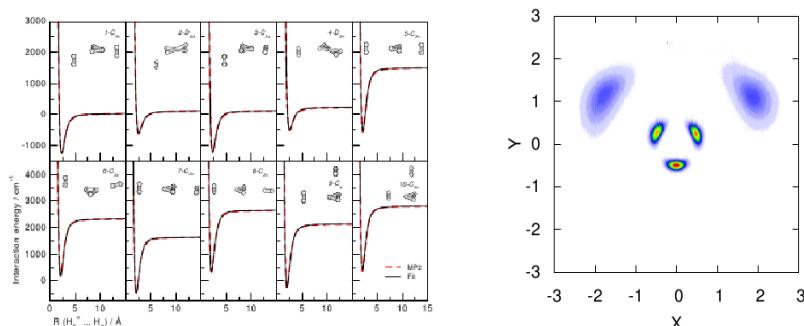
¹Instituto de Física Fundamental, CSIC, Serrano 123, 28006 Madrid, Spain

²Departamento de Química Física I, Facultad de Ciencias Químicas, Universidad Complutense de Madrid, 28040 Madrid, Spain

³Department of Chemistry and Cherry L. Emerson for Scientific Computation, Emory University, 1515 Dickey Drive, Atlanta, Georgia 30322, USA

E-mail: patricia@iff.csic.es

Full-dimensional ab initio potential energy surface is constructed for the H_7^+ cluster [1]. The surface is a fit to roughly 160000 interaction energies obtained with second-order Möller-Plesset perturbation theory (MP2) and the cc-pVQZ basis set, using the invariant polynomial method [2]. We employ permutationally invariant basis functions in Morse-type variables for all the internuclear distances to incorporate permutational symmetry with respect to interchange of H atoms into the representation of the surface. We describe how different configurations are selected in order to create the database of the interaction energies for the linear least squares fitting procedure. The root-mean-square error of the fit is 170 cm⁻¹ for the entire data set. The surface dissociates correctly to the $\text{H}_5^+ + \text{H}_2$ fragments. A detailed analysis of its topology (see Figure 1), as well as comparison with additional ab initio calculations, including harmonic frequencies, verify the quality and accuracy of the parameterized potential. This is the first attempt to present an analytical representation of the 15-dimensional surface of the H_7^+ cluster for carrying out dynamics studies [3]. Diffusion Monte-Carlo and Path Integral Monte-Carlo simulations are carried out for both H_7^+ and D_7^+ to obtain their ground vibrational states and thermal equilibrium states, respectively. Quantum vibrational zero point energy (ZPE) and dissociation energies for the reactions $\text{H}_7^+ \rightarrow \text{H}_5^+ + \text{H}_2$ and $\text{D}_7^+ \rightarrow \text{D}_5^+ + \text{D}_2$ are computed.



Left panel: 5 2D interaction energies for the $\text{H}_5^+ \dots \text{H}_2$ as a function of the intermolecular distance R connecting the centers of masses of the H_3^+ core (within the H_5^+), and the other H_2 . Right Panel: Projection of the probability density of H_7^+ on the H_7^+ plane at $T=10\text{K}$ as a function of the cartesian coordinates X e Y (in Angstroms).

[1] P. Barragán, R. Prosmitti, Y. Wang, and J.M. Bowman, J. Chem. Phys. 136, 224302 (2012).

[2] B.J. Braams and J.M. Bowman, Inter. Rev. Phys. Chem. 28, 577 (2009).

[3] P. Barragán, R. Pérez de Tudela, R. Prosmitti, C. Qu, and J.M. Bowman, J. Chem. Phys. In preparation (2013).

Why does C-O lengthen and C pyramidalize in the $n\pi^*$ state of formaldehyde? Expanding QTAIM to Excited States

David Ferro-Costas

¹Departamento de Química Física, Universidade de Vigo, Facultade de Química,

Lagoas-Marcosende s/n, 36310 Vigo, Galicia, Spain

E-mail: davidferro@uvigo.es

In the last years, the Quantum Theory of Atoms in Molecules (QTAIM) [1,2] has become an important tool in the world of the Quantum Chemistry, characterized for being more physically sound than other theories or models. In chemical literature this theory is, basically, used when an electronic ground state is taking into account. The results obtained are, in general, in line with the classical chemical intuition. Moreover, there is no evidence against extending its application to electronic excited states.

In this case, the excited state of formaldehyde associated to the 1 electron-transition from an O lone pair to a C-O σ^* MO is analyzed within the QTAIM framework, getting insight in 2 known effects (enlargement of the C-O bond and pyramidalization of the C atom) in terms of interactions defined through the own Hamiltonian and avoiding concepts more abstract like “antibonding orbitals” and “hybridation”. Fig. 1 shows the difference between excited and ground states electron densities and the representation of the QTAIM partitioning in both states.

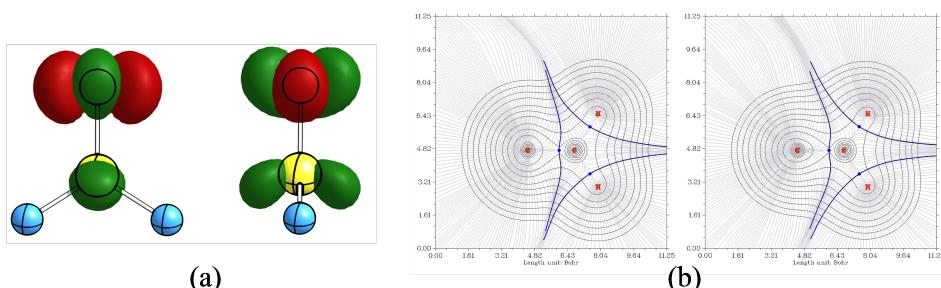


Figure 1: (a) Difference between the electron densities of the Excited and Ground states (isosurfaces of +0.025 au in green and -0.025 in red) and (b) Partitioning of the space in QTAIM basins for Ground and Excited states of formaldehyde.

[1] Bader, R. F. W. Chem. Rev., 91, 893-928 (1991).

[2] Bader, R. F. W. Atoms in Molecules. A Quantum Theory; International Series of Monographs in Chemistry. No 22. Oxford University Press. Oxford. (1990).

DNA base – Amino acid interactions: a theoretical study

J. González¹, I. Baños², E. J. Cocinero¹, J. A. Fernández¹ and J. Millán²

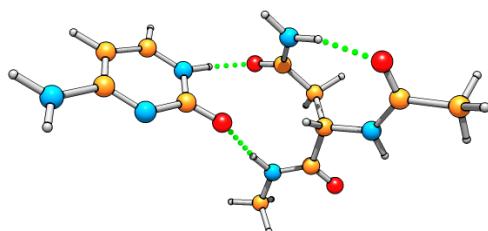
¹Dpto. Química Física, Facultad de Ciencia y Tecnología, Universidad del País Vasco-UPV/EHU, Bº Sarriena s/n, Leioa 48940, Spain. Fax: +34946013500; Tel: +34946015387;

²Dpto. Química, Facultad de Ciencias, Estudios Agroalimentarios e Informática,

Universidad de La Rioja, Madre de Dios, 51, Logroño 26006, Spain.

E-mail: jorge.gonzalezr@ehu.es

Several cellular mechanisms take place by DNA-protein interactions [1-4]. The recognition of a regulatory site is achieved due to the complementarity between the DNA and the protein structures and the specific contacts established by non-covalent interactions. Thus understanding fundamental processes, such as protein production and DNA/RNA transcription, requires of a deep knowledge of the forces governing the interactions. In this work we explore the conformational behaviour and different interactions for several DNA-protein systems using Density Functional Theory (DFT) calculations. Using a reductionist approach, the DNA-peptides interactions are divided in DNA base-amino acid pairs in order to reduce the complexity of the system, so higher calculation levels can be employed. Then, a first exploration of the conformational landscape of the bare molecules is carried out using molecular mechanics(MMFFs) [5], followed by DFT calculations (M06-2X/6-31+G(d) and M06-2X/6-311++G(d,p)⁶) on the most stable structures found. Once the monomers are fully characterized different combinations are explored, trying to rationalize the behaviour found in the real biological systems. We will present the results obtained for alanine, valine, isoleucine and asparagine; their analogous dipeptides, N-acetyl-L-Alanine-N-methylamide, N-acetyl-L-isoleucine-N-methylamide, N-acetyl-L-Valine-N-methylamide and N-acetyl-L-Asparagine-N-methylamide; and the cytosine – dipeptide complexes using the above-described methodology.



- [1] A.F.Jalbout, K.Y.Pichugin, L.Adamowicz; Eur. Phys. J. D 26; 197 (2003).
- [2] I. Galetich, S.G. Stepanian, V. Shelkovsky, M. Kosevich, L. Adamowicz; Mol. Phys. 100, 3649 (2002).
- [3] I. Galetich, S.G. Stepanian, V. Shelkovsky, M. Kosevich, Yu.P. Blagoi, L. Adamowicz; J. Phys. Chem. A 104, 8965 (2000).
- [4] R. Sathyaprya, M.S. Vijayabaskar, Saraswathy Vishveshwara; PLOS Comp. Bio. 4, e1000170 (2008).
- [5] T. A. Halgren; J. Comput. Chem. 20, 730 (1999)
- [6] Y. Zhao, G. D. Trhular; Acc. Chem. Res. 41, 157 (2008).

Theoretical Study on Dynamics of Fragmentation of L-Alanine²⁺

E. Rossich Molina¹, Y. Wang^{1,2}, M. Alcamí Pertejo¹, and F. Martin^{1,2}

¹ Departamento de Química, Módulo 13, Universidad Autónoma de Madrid, 28049 Madrid, Spain.

² Instituto Madrileño de Estudios Avanzados en Nanociencia (IMDEA-Nanociencia), Cantoblanco, Madrid, Spain
E-mail: estefania.rossich@uam.es

Nowadays, swift heavy ion beams have become a successfully alternative to traditional X-Ray radiation for cancer treatment. The ions have the advantage of being able to deposit the maximum energy at their Bragg peak on deep cancers minimizing the damage on healthy tissue. Therefore we are motivated to predict the fragmentation pathways of the biological molecule L-Alanine²⁺ (Ala) in gas phase after colliding with the energetic radiation and compare with future experimental measurements. Theoretical work on the dynamics of molecular fragmentations is important and can provide valuable information[1] which can not be obtained easily by experiments because this kind of processes take place in the scale of 1-100 fs. The energies of the orbitals of the neutral, singly and doubly charged Ala, as well as first and second Ionization Potentials were calculated. This information was used to obtain the Auger spectrum of Ala (see Fig. 1) which is to be compared with experiments. By performing BLYP/6-311++g(d,p) calculations on C-C bond breaking, we found low values of energy barriers. We also performed Car-Parrinello Molecular Dynamic [2] simulations on thermal fragmentation of Ala. Based on these results, Time Dependent DFT Molecular Dynamics simulations are planned to be done in the near future.

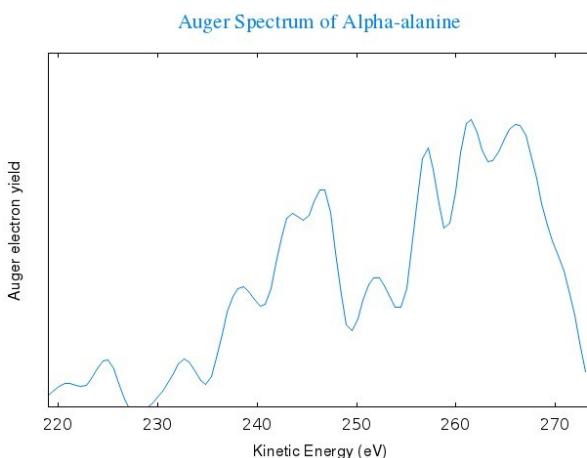


Figure 1: Theoretical Auger spectrum after ionization of carboxilic C1s.

[1] P.Lopez-Tarifa, M.A. Herve du Penhoat, R. Vuilleumier, I. Tavernelli, M-P. Gaigeot, J.P. Champeauz, A. Le Padellec, M. Alcamí, P. Moretto-Capelle, F. Martin and M-F. Politis, Phys. Rev. Lett, 107, 023202 (2011).

[2] R. Car, M. Parrinello, Phys. Rev. Lett, 55, 2471-2474 (1985).

Theoretical Study of the ionization and fragmentation of positively charged polycyclic aromatic hydrocarbons

C. Paris¹, S. Díaz-Tendero¹, M. Stener², M. Alcamí¹, and F. Martín^{1,3}

¹Departamento de Química, Facultad de Ciencias. Universidad Autónoma de Madrid. C/Fco. Tomás y Valiente 7, 28049 Cantoblanco, Madrid, Spain

²Dipartimento di Scienze Chimiche, Università di Trieste, Via L. Giorgieri 1, I-34127 Trieste, Italy

³Instituto Madrileño de Estudios Avanzados en Nanociencia(IMDEA-Nanociencia), Cantoblanco 28049 Madrid, Spain
E-mail: chiara.paris@uam.es

Polycyclic aromatic hydrocarbons (PAHs) are a class of organic molecules based on two or more fused aromatic rings. They are formed in a great variety of environments and some species have been found to be toxic and carcinogenic[1]. Interaction with low energy ions may constitute a unique tool for the identification of PAH isomers in the gas phase. Furthermore, PAH molecules are of important interest in the fields of astrophysics and astrochemistry[2] since they are considered as a significant component of interstellar dust and gas. They are also responsible for the emission features detected in interstellar IR spectra of many galactic and extragalactic sources. In the interstellar medium, PAH molecules are exposed to a variety of ionizing processes due to the presence of KeV ions in solar and stellar winds. Therefore it is interesting to study the interaction of PAHs with low-energy ions. More precisely, the fragmentation patterns of these molecules after interaction with low energy ions will provide information on their relative stability. With Density Functional Theory calculations we have studied the structure and stability of neutral and positively charged PAHs molecules. In particular we have considered four groups of molecules: (i) Anthracene, Acridine and Phenazine, (ii) C₁₈H₁₂ isomers: Benza[a]anthracene, Benza[c]anthracene, Chrysene, Triphenylene and Naphthacene, (iii) C₁₆H₁₀ isomers: Pyrene and Fluoranthene, (iv) Coronene. We investigated the vertical and adiabatic ionization potential, dissociation energies and the potential energy surface for the H/H⁺, 2H/H⁺H⁺, H₂/H₂⁺ loss channels for these molecules. Using the B3lyp functional, geometries were optimized with the 6-31+g(d) basis set. Frequency calculations were also carried out at the same level of theory. Single point energies were determined with the larger 6-311++g(3df,3pd) basis set and the same functional. In the present communication we will show our results and compare them with recent experimental measurements[3-7]. The latter allow us to better understand the fragmentation processes, the relative stability of each PAH molecule, the charge transfer and the energy deposited in the collision.

- [1] C.Bosetti,P. Boffetta, and C. La Vecchia, Ann. Oncol. 18, 431 (2007) .
- [2] A. G. G. M. Tielens, Ann.Rev. Astron. Astrophys. 46,289 (2008) .
- [3] A.I.S. Holm et al., J. ChemPhys 134, 04430 (2011) .
- [4] F. Seitz et al., J. Chem. Phys. 135 , 064302 (2011) .
- [5] H. A. B. Johansson et al., J. Chem. Phys. 135 , 084304 (2011) .
- [6] A. Lawicki et al. Phys. Rev. A 83, 022704 (2011) .
- [7] P. Rousseau and H. Zettergren , private communication .

Chemical reaction rate coefficients from Ring Polymer Molecular Dynamics

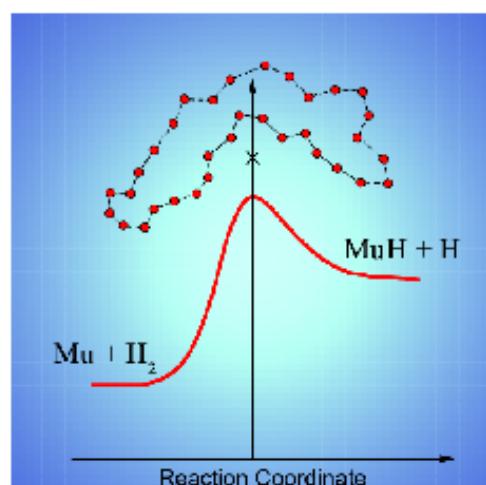
R. Pérez de Tudela¹, Y. V. Suleimanov², M. Menéndez¹ and F. J. Aoiz¹

¹Dpto. Química Física I, Facultad CC. Químicas, Universidad Complutense de Madrid, 28040 Madrid, Spain ²Dept. Chemical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, USA E-mail: ricperez@pas.ucm.es

We will present a new technique called Ring Polymer Molecular Dynamics (RPMD)[1-5] that allows the inclusion of quantum mechanical effects in classical molecular dynamics simulations. This method exploits the isomorphism between a quantum system and a classical system of fictitious ring polymers[6]. In particular, we used RPMD to compute rate coefficients in bimolecular gas-phase reactions. The main advantage of this methodology is that it can be extended to reactions involving more than three atoms in a straightforward way.

The first RPMD calculations carried out in our group involved muonium (Mu)[7], which in principle can be regarded as the most quantum atom. We found that for the Mu + H₂ reaction, RPMD results were in excellent agreement with exact QM calculations. Moreover, we could see that tunnelling is not a decisive quantum effect in this reaction. Instead, zero point energy effects (ZPE) are the ones that rule this dynamical process, an effect that this method is able to capture brilliantly. Next we were interested in studying the series of isotopologues of the H + H₂ reaction[8], in order to test the performance of RPMD. We were able to confirm a theoretical prediction made by Prof. Althorpe[9,10] by which RPMD should underestimate rate coefficients for symmetric reactions and overestimate them otherwise. We found that in order to assess for this symmetry, one must take into account the ZPE of both reactants and products. Thus, in our case, the only really asymmetric reaction of the family of isotopologues is the one involving the muonium atom. Only if ZPE effects are considered the prediction holds perfectly.

Finally we will show some results for two interesting reactions: O(³P) + HCl and Cl + O₃. The first one is another example of a highly asymmetric reaction, and the second one is an example of an application of the RPMD technique to bigger systems, indeed using a potential energy surface built in our group.



[1] I. R. Craig and D. E. Manolopoulos, J. Chem. Phys. 121, 3368 (2004)

[2] I. R. Craig and D. E. Manolopoulos, J. Chem. Phys. 122, 084106 (2005)

- [3] I. R. Craig and D. E. Manolopoulos, J. Chem. Phys. 123, 034102 (2005)
- [4] S. Habershon, D. E. Manolopoulos, T. E. Markland and T. F. Miller III, Ann. Rev. Phys. Chem. 64, 387 (2013)
- [5] R. Collepardo-Guevara, Y. V. Suleimanov and D. E. Manolopoulos, J. Chem. Phys. 130, 174713 (2009)
- [6] D. Chandler, J. Chem. Phys. 74, 4078 (1981)
- [7] R. Pérez de Tudela, F. J. Aoiz, Y. V. Suleimanov and D. E. Manolopoulos, J. Phys. Chem. Lett 3, 493 (2012)
- [8] Y. V. Suleimanov, R. Pérez de Tudela, P. G. Jambrina, J. F. Castillo , V Sáez-Rábanos, D. E. Manolopoulos and F. J. Aoiz, Phys. Chem. Chem. Phys., DOI: 10.1039/C2CP44364C (2013)
- [9] J. O. Richardson and S. C. Althorpe, J. Chem. Phys. 131, 214106 (2009)
- [10] C. Althorpe, J. Chem. Phys. 134, 114104 (2011)

Anomalous angular distributions in $H + D_2 \rightarrow H + HD$ reaction

D. Herraez-Aguilar¹, FJ Aoiz¹

¹Departamento de Química. Física,

Facultad de Química, Universidad Complutense, 28040 Madrid, Spain

E-mail: diegoherraez86@gmail.com

The Hydrogen-interchange reaction have drawn a great deal of effort since the early days of reaction dynamics. This does not mean, however, that our knowledge about the H₃ system is complete. Quite the contrary, its study continues rendering unexpected results whose applicability extends to other elementary collision processes. The minimum-energy path, in a collision between a hydrogen (H) atom and a deuterium (D(2)) molecule, is for the three nuclei to line up. Consequently, nearly collinear collisions cause HD reaction products to be backscattered with low rotational excitation, whereas more glancing collisions yield sideways-scattered HD products with higher rotational excitation[1]. However, recent studies[2] have shown that measured cross sections for the $H + D_2 \rightarrow H + HD(v' = 4, j')$ reaction at a collision energy of 1.97 electron volts contradict this behavior. The anomalous angular distributions match closely fully quantum mechanical calculations, and for the most part quasiclassical trajectory calculations. As the energy available in product recoil is reduced, a rotational barrier to reaction cuts off contributions from glancing collisions, causing high-j' HD products to become backward scattered. As the kinetic energy to overcome this barrier becomes limited, the three atoms adopt a nearly collinear configuration in the transition-state region to permit reaction, which strongly polarizes the resulting HD product[3]. These results are expected to be general for any chemical reaction in the low recoil energy limit.

[1] Félix Fernandez-Alonso, Brian D. Bean, Richard N. Zare, F. J. Aoiz, Luis Banares, and Jesus F. Castillo, *J. Chem. Phys.*, **115**, 4534, (2001).

[2] J. Jankunas J,RN. Zare, Bouakline F,SC. Althorpe SC,D. Herráez-Aguilar D, FJ. Aoiz.*Science*, **336**,1687-1690 (2012)

[3] J. Aldegunde, D. Herraez-Aguilar, P. G. Jambrina, F. J. Aoiz, J. Jankunas, and R. N. Zare, *J. Phys. Chem. Lett.*, **3**, 2959-2963 (2012)

Quantum control with the non-resonant Stark effect: manipulating the singlet-triplet transition in ion strings

P. Vindel-Zandbergen¹, B.Y.Chang¹, I.R.Sola¹, Mirjam Falge², Volker Engel² and Manfred Lein³

¹Departamento de Química Física I. Universidad Complutense de Madrid. 28040 Spain

²Institut fur Physikalische und Theoretische Chemie. 97074 Würzburg, Germany

³Leibniz Universität Hannover. Institut fr Theoretische Physik, 30167 Hannover

E-mail: p.vindel.zandbergen@gmail.com

The control of chemical reactions by means of ultrashort laser pulses is an area of great interest. Over the past years significant developments have been made in using the quantum properties of light and matter to control the dynamics of molecular processes[1]. Using the properties of quantum interference we can achieve an unprecedent degree of control over the dynamics from simple atomic systems to complex biological molecules.

As a first approximation, we can view the control as the quest of frequencies and intensities of a laser pulse or a sequence of laser pulses that lead us to the desired products. For this end, multiple control schemes have emerged in which the laser can “drive” the system[2]. The non-resonant dynamic Stark effect (NRDSE) scheme is a simple but very general method that uses non-resonant electromagnetic fields to induce large time-dependent Stark-shifts in the energy levels. This scheme is used in many current experiments to hold and align molecules, to shape potential energy surfaces, influencing the outcome of photodissociation reactions at conical intersections[3]. As an interesting application of the NRDSE it is significant the optical control of the singlet-triplet transition, where the scheme is used to efficiently couple or decouple an intramolecular process that is not directly affected by the light [4].

In the present work, the NRDSE scheme is implemented to control the singlet-triplet transitions in a simple but very general model. The Shin-Metiu-Engel Hamiltonian[5,6] models the behavior of two electrons in an ion string with one moving ion, including spin exchange interactions between the singlet and triplet states. In spite of the simplicity of forcing one-dimensional (aligned) particle motion in screened Coulomb potentials, the model permits evaluating different levels of approximations. We implement the NRDSE scheme to stop or force the singlet-triplet transition working with very few potentials, with a large set of electronic potentials within the Born-Oppenheimer approximation, and by a full 3D Quantum propagation, including non-adiabatic couplings.

[1] R.S.Judson, H.Rabitz. Phys. Rev. Lett.68,1500-1503. (1992)

[2] P.Brumer, M.Shapiro. Chemical Physics Letters.,126, 541-546. (1986)

[3] Benjamin J.Sussman, Dave Townsend, Misha Yu. Ivanov and Albert Stolow. Science, 314, 278-281. (2006)

[4] Jesús González-Vázquez, Ignacio R. Sola, Jesús Santamaría and Vladimir S.Malinovsky. J.Chem.Phys,125,124315. (2006)

[5] S.Shin, H.Metiu.J.Chem.Phys,102,9285-9295. (1995)

[6] M.Erdmann, E.K.U.Gross, V.Engel.J.Chem.Physics,121,9666-9670. (2004)

Rotational spectra and ab initio modeling of monolignols

M. Vallejo López¹, P. Écija², E. J. Cocinero², A. Lesarri¹, J. A. Fernández², F. Basterretxea², F. Castaño²

¹Departamento de Química Física y Química Inorgánica, Facultad de Ciencias,
Universidad de Valladolid, 47001, Valladolid (Spain)

²Departamento de Química Física, Facultad de Ciencia y Tecnología, Universidad del País
Vasco (UPV-EHU), Apartado 644, 48080 Bilbao (Spain)

E-mail:

Monolignols are natural chemicals occurring in plants and source materials for biosynthesis of lignans and lignin [1]. This family includes several methoxyphenols like coniferyl alcohol (CA), sinapyl alcohol (SA) and para-coumaryl alcohol (p-CA), which may form biopolymers of industrial interest in the preparation of alcohols, sugars and paper. We have initiated a conformational and structural study of several monolignols using Fourier transform microwave (FT-MW) Spectroscopy in a supersonic jet expansion. In this work we report the experimental results for coniferyl alcohol, for which only a low-resolution Raman spectrum was previously available [2]. Because of the large number of molecular conformations which may arise by the three ring substituents the experimental study was supplemented by ab initio calculations describing the conformational landscape, rotational parameters and interconversion barriers. All conformations within an energy window of 8 kJ mol⁻¹ are reported using MP2 and the M06-2X DFT model. The rotational spectrum detected the presence of a single most stable conformation, for which accurate rotational and centrifugal distortion parameters have been determined. The rotational parameters were found in good agreement with the predictions for the global minimum. The non-observation of additional conformations has been rationalized in terms of magnitude of the collisional relaxation barriers.

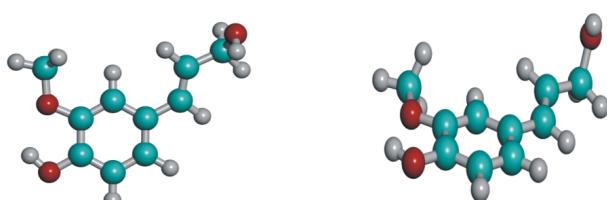


Figure 1. Detected conformation of coniferyl alcohol.

[1] a) Y. Chen, S. Sarkanen. Phytochemistry 71, 453-462, 2010. b) L. K. Takahashi, J. Zhou, O. Kostko, A. Golan, S. R. Leone, M. Ahmed. J. Phys. Chem. A 115, 3279-3290, 2011.

[2] M. Kihara, M. Takayama, H. Wariishi, H. Tanaka. Spectrochimica Acta part A 58, 2213-2221, 2002.

Two-step condensation of the charged Bose gas

R. L. Delgado¹, P. Bargueño², and F. Sols²

¹Dep. Física Teórica I, Universidad Complutense de Madrid (UCM)

²Dep. Física de Materiales, Universidad Complutense de Madrid (UCM)

E-mail: rafael.delgado@madrimasd.net

The condensation of the spinless ideal charged Bose gas in the presence of a magnetic field is revisited. The conventional approach is extended to include the macroscopic occupation of excited kinetic states lying in the lowest Landau level, which plays an essential role in the case of large magnetic fields. In that limit, signatures of two diffuse phase transitions (crossovers) appear in the specific heat. In particular, at temperatures lower than the cyclotron frequency, the system behaves as an effectively one-dimensional free boson system, with the specific heat equal to $\frac{1}{2}Nk_B$ and a gradual condensation at lower temperatures.

[1] R. L. Delgado, P. Bargueño and F. Sols, Phys. Rev. E 86, 031102 (2012)

Posters

Vibrationally resolved k-shell photoionization spectrum of BF_3

D. Ayuso¹, author² K. Sakai⁴, E. Plésiat¹, M. Patanen², L. Argenti¹, K. Kooser³, O. Travnikova², M. Kimura⁴, S. Mondal⁴, A. Palacios¹, E. Kukk³, P. Decleva⁵, K. Ueda⁴, F. Martín¹, and C. Miron²

¹Departamento de Química, Módulo 13, Universidad Autónoma de Madrid, Cantoblanco
28049 Madrid, Spain

²Synchrotron SOLEIL, L'Orme des Merisiers, Saint-Aubin, BP48, 91192 Gif-sur-Yvette
Cedex, France

³Department of Physics and Astronomy, University of Turku, FI-20014 Turku, Finland

⁴Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, Senday
980-8577, Japan

⁵Dipartimento di Scienze chimiche, Università di Trieste, IT-34127, and CNR-IOM,
Trieste, Italy

⁶Instituto Madrileño de Estudios Avanzados en Nanociencia (IMDEA-Nanociencia),
Cantoblanco, ES-28049 Madrid, Spain
E-mail: david.ayuso@uam.es

We present our latest results in the study of inner shell photoionization of boron trifluoride (BF_3), where an electron is ejected from boron 1s orbital. vibrationally resolved cross sections (CS) have been computed within the Born-Oppenheimer approximation using first order perturbation theory. Dipole couplings between the ground state of the neutral molecule and all possible final states have been calculated employing the B-spline static-exchange Multi-Body Density Functional Theory (MB-DFT) method [1–3], which makes use of the Kohn-Sham DFT to describe the molecular ionic states and of the Garlekin approach to evaluate continuum electron wave functions in the field of the corresponding Kohn-Sham density. The nuclear motion is taken into account by solving the time independent Schrödinger Equation (TISE) for the totally symmetric vibrational mode.

Boron 1s vibrationally resolved photoelectron spectrum of BF_3 has been measured at the PLÉIADES beamline [4] at SOLEIL (France) in the photon energy range of 200 eV – 600 eV. vibrationally resolved photoelectron ratios feature clear oscillations with respect to the photon energy due to intramolecular scattering. Experimental data are in good agreement with our theoretical calculations and with a first-Born approximation model [5,6].

- [1] M. Stener, G. Fronzoni and P. Decleva, Chem. Phys. Lett. 351, 469–474 (2002)
- [2] M. Stener and P. Decleva, J. Chem. Phys. 112, 10871 (2000)
- [3] D. Toffoli et al., Chem. Phys. 276, 2543 (2002)
- [4] <http://www.synchrotron-soleil.fr/Recherche/LignesLumiere/PLEIADES>
- [5] E. Plésiat et al., Phys. Rev. A 85, 023409 (2012)
- [6] L. Argenti et al., New J. Phys. 14, 033012 (2012)

Caracterización espectroscópica de los fármacos indometacina y ketorolac en disolución acuosa

E. Corda^{2,1}, P. Sevilla^{1,2}, M. Hernández², J. V. García-Ramos¹, C. Domingo¹

¹Dep. Química Física II, Facultad de Farmacia, UCM, 28040 Madrid

²Instituto de Estructura de la Materia, IEM-CSIC, Serrano 121, 28006 Madrid

E-mail: elisacorda@hotmail.it

Los fármacos antiinflamatorios no esteroideos (NSAID en inglés) son sustancias químicas con efecto antiinflamatorio, analgésico y antipirético. En este trabajo se ha llevado a cabo la obtención y análisis de los espectros de absorción UV-visible, de fluorescencia y Raman de los fármacos antiinflamatorios no esteroideos indometacina (IM) y ketorolac (KT) en disolución acuosa para diferentes condiciones experimentales [1-2]. Asimismo, se han estudiado los correspondientes compuestos en presencia de coloide de nanopartículas de plata, buscando las condiciones experimentales óptimas en las que se puedan obtener espectros amplificados por superficies metálicas SERS y/o SEF de IM y/o KT. La caracterización espectroscópica aporta datos relevantes acerca de las propiedades fisicoquímicas de ambos fármacos y supone el paso previo y necesario al diseño de nuevas formas de administración que permitan una liberación local y controlada para minimizar los efectos secundarios de dichos fármacos. Con este propósito, siguiendo el protocolo puesto a punto para el fármaco antitumoral emodina [3], se han hecho los primeros ensayos de incorporar los complejos IM/Ag y/o KT/Ag a una matriz de silicio poroso [4].

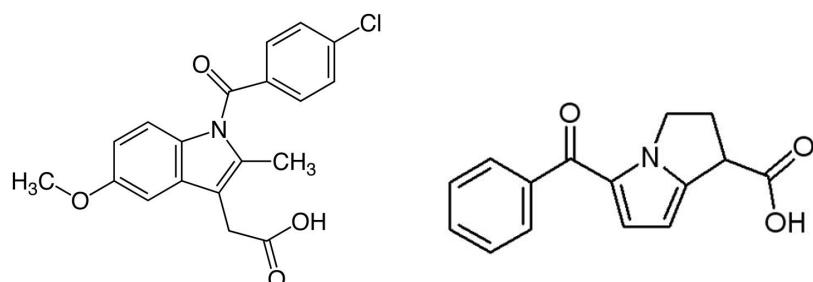


Figura 1: Estructuras moleculares de indometacina (izquierda) y ketorolac (derecha)

- [1] A. C. Weedon, D. F. Wong, , J. Photochem. Photobiol. A-Chem. 61, 27-33 (1991).
- [2] S.K. Basu, K. Kavitha, M. Rupeshkumar, Sci. Pharm. 78, (2010).
- [3] Hernández M., Recio G., Martín-Palma R. J., García-Ramos J. V., Domingo C., Sevilla P., Resúmenes de las comunicaciones presentadas a la X RNO, Zaragoza (2012).
- [4] Salonen J., Laitinen L., Kaukonen A. M., Tuura J., Bjorkqvist M., Heikkila T., Vahakinkila K., Hirvonen J., Lehto V. P., J. Control. Release 108, 362-374 (2005).

Chaos and macroscopic superpositions in a driven Bose gas

Martin Heimsoth¹, Charles E. Creffield¹, Lincoln D. Carr², Fernando Sols¹

¹*Departamento de Física de Materiales, Universidad Complutense de Madrid, E-28040, Madrid, Spain*

²*Department of Physics, Colorado School of Mines, Golden, Colorado 80401, USA*

E-mail: heimsoth@ucm.es

We study the dynamics of a Bose-Einstein condensate subject to a weak perturbational driving potential. The here considered system can effectively be described by a three-mode Hamiltonian within a many-body framework [1,2]. In this contribution, we will focus on the regime, in which a mean-field approximation predicts chaotic motion. A many-body simulation in this regime reveals that the observation of chaotic motion within mean-field indicates the failure of this approximation. This can be seen by a rapid decrease of the condensate wave-function, defined as the maximally occupied eigenstate of the reduced density matrix. Even more, the occupation numbers become highly correlated, what suggests the possible creation of macroscopic superposition states in the classically chaotic regime.

[1] M. Heimsoth C. E. Creffield, L. D. Carr, F. Sols, New J. Phys. 14, 075023 (2012)

[2] M. Heimsoth C. E. Creffield, F. Sols, Phys. Rev. A 82, 023607 (2010)

Fragmentation dynamics of excited amino acids in gas phase: glycine and β -alanine

D. G. Piekarski¹, S. Díaz-Tendero¹, F. Martín^{1,2}, M. Alcamí¹

¹Departamento de Química. Facultad de Ciencias. Universidad Autónoma de Madrid. C/Fco. Tomás y Valiente 7. 28049. Cantoblanco. Madrid. Spain.

²Instituto Madrileño de Estudios Avanzados en Nanociencia (IMDEA-Nanociencia),
Cantoblanco, 28049 Madrid, Spain

E-mail: derwiszck@gmail.com

Glycine (Gly) and β -alanine (β -Ala) are the simplest amino acids but not less important than the others. For example β -Ala is a component of coenzyme A (in pantothenic acid) and carnosine, the latter of which has been proven to possess antioxidant properties, it can inhibits the action of free radicals[1,2] and also retard cancer growth in animal models[3]. Moreover, it has been shown that oxidative reactions occurred in amino acids could damage their structure and in consequence develop diseases like Alzheimer[4]. Ion-biomolecule collisions has become a fundamental technique to study radiation damage of biological tissues. Changes in the biomolecules are not caused directly by ion-beam radiations but by radicals and ions created after fragmentation of amino acids along the ionisation path[5,6]. Therefore, it is very important to get a deep knowledge of their structures, stability and fragmentation after ionisation. Moreover, it is important to understand the fragmentation mechanisms and the role of transient species. Using Quantum Chemistry methods we have evaluated the structure and stability of neutral and ionized Gly and β -Ala aminoacids in gas phase. Molecular Dynamics calculations using ADMP method [7] allow us to propose different mechanisms arising in excited charged aminoacids: ultrafast proton transfer and Coulomb explosion appear in competition. Within the framework of the Density Functional Theory we have explored the potential energy surface (PES) and computed ionisation potentials and relative energies (ΔE) for neutral and cationic isomers of Gly and β -Ala and compared with previous studies[8,9,10]. We found many additional stable conformers of Gly and β -Ala. Some of the obtained Gly and β -Ala dication conformers suffered Coulomb explosion but we also found minima in the PES. Four isomers of β -Ala are 5-membered ring compounds (with O – N bonds) and the others are open structures, where an intramolecular proton transfer leads to different atomic rearrangement. This kind of cyclic structures has not been found for cationic conformers of bigger amino acids like γ -aminobutyric acid (GABA)[11]. In this poster we will present our results and compare them with experimental measurements[12,13], which allow us to better understand charge transfer, energy deposit and fragmentation processes in ion-biomolecule collision experiments.

- [1] O. I. Aruoma, M. J. Laughton, B. Halliwell, Biochem J., 264(3): 863–869 (1989) .
- [2] S. Y. Choi, et. all, Biochimica et Biophysica Acta 1472, 651-657 (1999).
- [3] Ch. Renner, N. Zemitzsch et al, Molecular Cancer, 9.2,(2010).
- [4] D. A. Butterfield, D. Boyd-Kimbal, Biochimica et Biophysica Acta 1703, 149,(2005).
- [5] L. Sanche, Eur. Phys. J. D, 35, 367., (2005).
- [6] D. Schardt, T. Elsässer, D. Schulz-Ertner, Rev. Mod. Phys., 82, 483-495, (2010).

- [7] Iyenagar, S. S.; Schlegel, H. B.; Voth, G. A. *J. Phys. Chem. A.*, 107, 7269-7277, (2003).
- [8] A. Gil, S. Simon, et. all, *J. Chem. Theory Comput.*, 3, 2210-2220., (2007).
- [9] A. G. Császár, *J. Am. Chem. Soc.*, 114, 9568-9575., (1992).
- [10] M. E. Sanz, A. Lesarri, M. I. Peña, *J. Am. Chem. Soc.*, 128, 3812-3817., (2006).
- [11] M. Capron, S. Díaz-Tendero, S. Maclot et al, *Chem. Euro. J.*, (2012).
- [12] S. Maclot et al, *Chem Phys Chem*, 12, 930-936., (2011).
- [13] S. Maclot, A. Domaracka, P. Rousseau et al, private communication.

Fluorescence characterization of a drug delivery system based on a nanostructured porous silicon matrix loaded with the anti-tumoral drug emodin adsorbed on silver nanoparticles

M. Hernández¹, G. Recio², R.J. Martín-Palma², V. Torres-Costa², J.V. García-Ramos¹, C. Domingo¹, P. Sevilla^{1,3}

¹*Instituto de Estructura de la Materia, IEM-CSIC, Serrano 121, 28006-Madrid, Spain.*

²*Dep. Física Aplicada, F. Ciencias, UAM, 28049-Madrid, Spain.*

³*Dep. Química Física II, F. Farmacia, UCM, 28040-Madrid, Spain.*

E-mail: marga@iem.cfmac.csic.es

Porous silicon (PS) (fig.1) is an interesting biocompatible and biodegradable material, able to carry biomolecules conjugated to drugs for achieving site-specific delivery acting as a “magic bullet”. These properties make nanostructured-PS microparticles suitable candidates for developing novel drug delivery systems. However, in most cases the drug does not enter inside the pores, being then necessary to functionalize the silicon surface.

To overcome this limitation we have tried a different approach, loading the PS matrix with the drug emodin adsorbed on a silver colloid. This emodin-silver set has been previously spectroscopically characterized in our group [1, 2]. The use of noble metal nanoparticles presents a double advantage. First, drug molecules can be adsorbed on their surfaces and, consequently, transported together; secondly, and very important, the excitation of Localized Surface Plasmon Resonances (LSPRs) on metal nanoparticles makes them excellent sensors using SERS and SEF spectroscopy.

The setting up and optimization of these new systems pass through the characterization of their physicochemical behaviour. We have accomplished it using fluorescence and Raman spectroscopy.

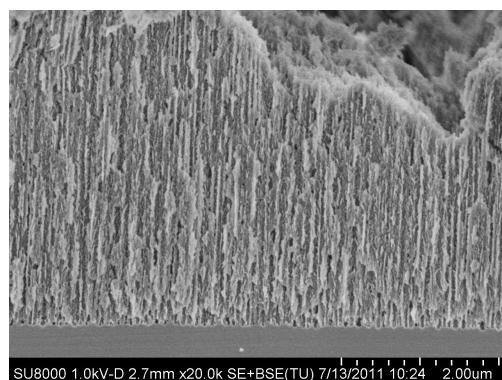


Figure 1: SEM images of porous silicon matrix showing the size of the pores (62.0 nm).

- [1] P. Sevilla, F. García-Blanco, J.V. García-Ramos and S. Sánchez-Cortes, Phys. Chem. Chem. Phys., 11, 8342, (2009).
- [2] R. De-Llanos, S. Sánchez-Cortés, C. Domingo, J. V. García-Ramos and P. Sevilla, J. Phys. Chem. C, 115, 12419 (2011).

Energy Distributions of Neutrals and Ions in H₂ Low Temperature Plasmas

M. Jiménez-Redondo, I. Tanarro, E. Carrasco, and V.J. Herrero

¹*Instituto de Estructura de la Materia (IEM-CSIC), Serrano 123, 28006 Madrid (Spain)*

E-mail: m.jimenez@csic.es

In this work, we analyse the results obtained by visible emission spectroscopy, energy resolved ion mass spectrometry and electric probes on H₂ plasmas generated in low pressure hollow cathode glow discharges. The study allows determining the energy distributions shown by the different plasma constituents, which span five orders of magnitude. So, the rotational H₂ temperature, assumed to be close to the translational one, scarcely exceeds the room temperature (0.03 eV); free electrons, responsible of primary ionization and dissociation processes, display mean kinetic energies of 3-6 eV; whereas ions (H⁺, H₂⁺, H₃⁺) and even a part of the H atoms are found at the highest energy limit (>300 eV). Our present study focuses on the line-shape analysis of the H Balmer series emitted by the plasma, whose spectral profiles evince its remarkable deviation from thermal equilibrium, and on the dependence of these profiles with H₂ pressure. The aim is to get a deeper understanding of the processes responsible of this behavior, presently an issue under some controversy. The technique has been proposed to detect nanoparticles formation in plasmas. The results may be also of interest for the spectral diagnostics of the atmospheres of the outer planets. Three different Doppler broadenings are found in the atomic lines (fig.1): the narrow peak (a), the plateau (b) and the far wings (c), with FWHM of some 0.3, 6 and up to 80 eV, respectively. Besides, a directional and asymmetric behavior in the line shifts up to some 300 eV is observed when ions are directed towards the observation window. The narrow line peak can be explained by direct electron impact excitation of the free H atoms and by Frank-Condon transitions to Rydberg levels. The plateau is explained by excitations to pre-dissociative levels and levels giving rise to dissociative ionization. Their effectiveness depends on electron temperature. On the contrary, the far wings are assumed to be due mainly to charge transfer reactions and dissociative reactions of the H⁺, H₂⁺ and H₃⁺ ions with H₂, as well as to backscattering of H atoms after ionic neutralizations in the walls. These latest processes depend on the collision frequency and pressure. The ion energy distributions obtained by mass spectrometry and the electron temperatures measured with the electric probe support the validity of the proposed processes.

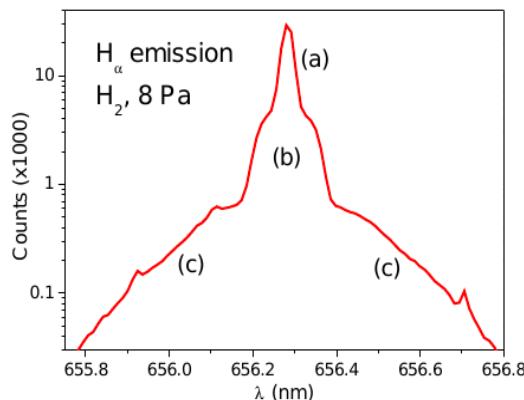


Figure 1: Spectral profile of the emitted H_α Balmer line from a 8 Pa, 150 mA, 450 V, hollow cathode discharge, detected with a visible spectrometer. Spectral resolution: 0.02 nm.

UV laser desorption/ionization of polymers and peptides assisted by Platinum Nanoparticles synthesized by Laser Ablation in Water.

Maite Cueto¹, F. Gámez², A. R. Hortal², P. Hurtado², B. Martínez-Haya² M. Sanz³, M. Oujja³, M. Castillejo³

¹Instituto de Estructura de la Materia (IEM-CSIC), Serrano 123, 28006 Madrid (Spain)

²Departamento de Sistemas Físicos, Químicos y Naturales, Universidad Pablo de Olavide, 41013 Seville (Spain)

³Instituto de Química Física Rocasolano (CSIC), Serrano 119, 28006 Madrid (Spain)

E-mail: maite.cueto@iem.cfmac.csic.es

We have investigated benchmark laser desorption/ionization mass spectroscopy processes assisted by platinum nanoparticles (NALDI-MS). The technique has been applied to the detection of a synthetic polymer (polyethylenglycol PEG600) and a peptide (Angiotensin I). Platinum stands out among the noble metals as a NALDI active substrate because of its low heat conductivity and high melting temperature [1]. It has been shown that stable platinum nanoparticles suitable for NALDI can be prepared by laser ablation in water solutions [2,3]. In this work, we use aqueous suspensions of platinum colloidal nanoparticles of varying size, shape, crystallinity and polydispersity produced in solution by ablation with a Q-switched Nd:YAG laser at several laser wavelengths (1064, 532 and 266 nm) and stabilizing agents, such as PEG, PVA, PVP and citrate. NALDI-MS measurements in positive-ion mode were performed in a commercial time-of-flight mass spectrometer (UltrafleXtreme, Bruker), employing 355 nm nanosecond laser pulses from a Nd:YAG laser at a 1 kHz repetition rate. Good sensitivity is obtained for the detection of both PEG600 and Angiotensin I. For PEG600 the LDI spectra display adducts associated with the cationization by Na⁺ or K⁺, whereas for the Angiotensin the protonated peptide is detected along with the cationized adducts, with relative intensities depending on the surfactant employed. The best overall NALDI-MS performance was found for nanoparticles of average size 4 nm, produced with 532 nm laser pulses in the presence of sodium citrate as surfactant.

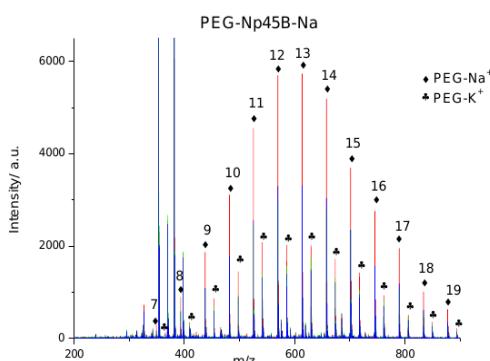


Figure 1: Typical NALDI TOF-MS of PEG600 with Pt nanoparticles as active substrate

[1] T. Yonezawa, H. Kawasaki, A. Tarui, T. Watanabe, R. Arakawa, T. Shimada, F. Mafuné, Analytical Sciences, 25 (3), 339-347 (2009).

[2] W. T. Nichols, T. Sasaki, N. Koshizaki, Journal of Applied Physics, 100, 114911-114913 (2006).

[3] M. Cueto, M. Sanz,, M. Oujja, F. Gámez, B. Martínez-Haya, M. Castillejo, Journal of Physical Chemistry C, 115, 22217–22224 (2011)

Relevancia de superficies atmosféricas en la eliminación de sustitutos de CFCs, $\text{CF}_3\text{CH}_2\text{OH}$.

E. Moreno¹, A. Aranda² y Y. Díaz-de-Mera²

¹ Departamento de Física Molecular, Instituto de Estructura de la Materia, CSIC, Madrid

¹ Dpto. de Química-Física, Facultad de Ciencias y Tecnologías Químicas, UCLM, CIUDAD REAL

E-mail: Elena.moreno@csic.es

Recientemente se ha descubierto que los procesos atmosféricos heterogéneos pueden suponer una importante vía de eliminación o de almacenamiento de diferentes contaminantes en la atmósfera. Actualmente, unos contaminantes de interés atmosférico son los nuevos sustitutos de los CFCs, compuestos que forman parte de refrigerantes, agentes espumantes, disolventes [1,2].

Es necesario cuantificar dichos procesos atmosféricos para entender el impacto de redistribución de estos contaminantes en la alta troposfera y sobre las nubes tipo cirrus que existen en esta región. Para contribuir a dicha cuantificación, en este trabajo se han estudiado los procesos de interacción entre $\text{CF}_3\text{CH}_2\text{OH}$ (sustituto de CFCs) y superficies de hielo (agua pura) y de hielo dopado (soluciones acuosas acidificadas de HNO_3).

Para llevar a cabo los estudios, se ha empleado un reactor de tubo de flujo acoplado a un espectrómetro de masas. Las superficies de hielo son expuestas a diferentes concentraciones del gas traza, obteniéndose las correspondientes isotermas de adsorción. La evolución de la capacidad de la monocapa se aproxima al modelo de Langmuir [3] como se representa en la siguiente figura 1.

De este estudio se obtienen parámetros de adsorción y parámetros termodinámicos que pueden ser empleados para diferentes evaluaciones atmosféricas y para completar modelos atmosféricos.

Figura 1: Isotermas de adsorción de $\text{CF}_3\text{CH}_2\text{OH}$ sobre hielo puro. (Temperaturas del estudio. 203K (red dots), 206K (blue), 216K (green) y 223K (pink). Error de 10 % en Nads y error de 5 % en $[\text{CF}_3\text{CH}_2\text{OH}]$).

[1] Chen, L.; Takenaka, N.; Bandow, H., y Maeda, Y. *Atmospheric Environment* 37(34), 4817-4822, (2003).

[2] Rajakumar, B.; Burkholder, J.B., Portmann, R.W. y Ravishankara, A.R. *Physical Chemistry Chemical Physics*, 7, 2498-2505, (2005).

[3] Langmuir, I. *Journal of the American Chemical Society*, 40, 1361-1403, (1918).

Global potential energy surface of H₄⁺ system. Reactive collisions using QCT

Cristina Sanz Sanz

Institute for Fundamental Physics. CSIC, C/Serrano 113Bis. Office 213, 28006 Madrid
(Spain) *E-mail:* cristina.sanz@csic.es

H₄⁺ is an important molecule in astrophysics because together with its isotopologues are involved in reactions of formation of H₃⁺, the most abundant ion in space. We have calculated the first global potential energy surface for the ground electronic state of H₄⁺ based on ab initio calculations. All studies of this system in the literature have made use of a DIM potential. The reaction of H₂ + H₂⁺ → H₃⁺ + H is an exothermic reaction with an energy of -1.81eV. The equilibrium geometry of H₄⁺ can be seen as an isosceles H₃⁺ with the fourth proton bound to the vertex created with the two elongated distances. The energy of the H₄⁺ is its equilibrium is about 2eV below the entrance channel, H₂ + H₂⁺. In addition, H₄⁺ system presents a crossing between the ground and the first excited state in the entrance channel due to the equally probable position of the charge in either diatomic molecule. The crossing is produced when both molecules have the same interatomic distance. The lowest crossing in energy is obtained just above the first excited vibrational state of H₂ and the second excited vibrational state of H₂⁺. The study of dynamics considering reactants in higher vibrational excited states than the ground state needs to treat this crossing to properly describe the position of the charge. In the literature the most common method describing the entrance channel is surface hoping.

In this contribution I will show as well the preliminary results obtained for the reactive collisions of H₂ + H₂⁺ using quasiclassical trajectories. Results have been compared with other theoretical studies, which used the DIM potential approach, and with the available experimental studies in literature.

List of Participants

Corrales Castellanos, María Eugenia
`me.corrales@quim.ucm.es`
Universidad Complutense de Madrid
Madrid

González González, Marta
`marta.glezglez@hotmail.com`
Universidad Complutense de Madrid
Madrid

Heimsoth, Martin
`heimsoth@fis.ucm.es`
Universidad Complutense de Madrid
Madrid

Rodríguez Díaz, Javier
`javier.rodriguez.diaz@quim.ucm.es`
Universidad Complutense de Madrid
Madrid

Balerdi Villanueva, Garikoitz
`garikoitz.bv@gmail.com`
Universidad Complutense de Madrid
Madrid

M. Vallejo López
`montse.vallejo@qf.uva.es`
Universidad de Valladolid
Valladolid

Elena Moreno Atahonero
`Elena.moreno@csic.es`
Instituto de Estructura de la Materia, CSIC
Madrid

Rui E. F. Silva
`rui.silva@uam.es`
Universidad Autonoma de Madrid
Madrid

David Ayuso
david.ayuso@uam.es
Universidad Autónoma de Madrid
Madrid

Maite Cueto
maite.cueto@iem.cfmac.csic.es
Instituto de Estructura de la Materia (IEM-CSIC)
Madrid

Ignacio López
ilopez@iqfr.csic.es
Instituto de Química Física Rocasolano, CSIC
Madrid

Estefanía Lopez
estefania.lopez.marne@gmail.com
University of Barcelona
Barcelona

Silvia Acosta-Gutiérrez
silviaa.gutierrez@gmail.com
Universidad de La Laguna
La Laguna

Humberto Jr. Silva
humberto.silva@uam.es
Universidad Autónoma de Madrid
Madrid

Maitreyi Robledo
maitreyi.robledo@uam.es
Universidad Autónoma de Madrid
Madrid

Rocio Rodríguez-Cantano
rrcantano@iff.csic.es
Institute of Fundamental Physics, IFF-CSIC
Madrid

Virginia Ovejas
virginia.ovejas@ehu.es
Universidad del País Vasco (UPV/EHU)
Bilbao

Marta Fernández-Fernández
martafernandez051@ikasle.ehu.es
Universidad del País Vasco (UPV/EHU)
Bilbao

Patricia Écija
patricia.ecija@ehu.es
Universidad del País Vasco (UPV-EHU)
Bilbao

Imanol Usabiaga
usabiagakie@hotmail.com
Universidad del País Vasco UPV/EHU
Bilbao

Estíbaliz Méndez
estibaliz.mendez@ehu.es
Universidad del País Vasco (UPV/EHU)
Leioa

Roberto Antonio Fernández
Robertoantonio.fernandez@ehu.es
Universidad del país vasco
Leioa

Alexandre Zanchet
zanchet@iem.cfmac.csic.es
Instituto de Estructura de la materia, C.S.I.C.
Madrid

Alba María Jorge
alba.jorge@uam.es
Universidad Autónoma de Madrid
Madrid

Patricia Barragán
patricia@iff.csic.es
Instituto de Física Fundamental, CSIC
Madrid

David Ferro-Costas
davidferro@uvigo.es
Universidade de Vigo
Vigo

Jorge González
jorge.gonzalezr@ehu.es
Universidad del País Vasco-UPV/EHU
Leioa

Estefanía Rossich Molina
estefania.rossich@uam.es
Universidad Autónoma de Madrid
Madrid

Chiara Paris
chiara.paris@uam.es
Universidad Autónoma de Madrid
Madrid

Ricardo Perez Tudela
ricperez@pas.ucm.es
Universidad Complutense de Madrid
Madrid

Diego Herráez
diegoherraez86@gmail.com
Universidad Complutense de Madrid
Madrid

Patricia Vindel-Zandbergen
p.vindel.zandbergen@gmail.com
Universidad Complutense de Madrid
Madrid

Rafael Delgado López
rafael.delgado@madrmasd.net
Universidad Complutense de Madrid
Madrid

Elisa Corda
elisacorda@hotmail.it
Universidad Complutense de Madrid
Madrid

Dariusz G. Piekarski
derwiszck@gmail.com
Universidad Autónoma de Madrid
Madrid

Juan J. Nogueira
juanjonog@hotmail.com
Université Bordeaux
France

Margarita Hernández Gonzalez
marga@iem.cfmac.csic.es
Instituto de Estructura de la Materia, IEM-CSIC
Madrid

M. Jiménez-Redondo
m.jimenez@csic.es
Instituto de Estructura de la Materia (IEM-CSIC)
Madrid

Cristina Sanz
cristina.sanz@csic.es
CSIC
Madrid

Estefanía Fernández
tfyfdez@gmail.com
Universidad Autonoma de Madrid
Madrid